CRANFIELD UNIVERSITY

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A METHODOLOGICAL APPROACH TO PROCESS INTENSIFICATION

SCHOOL OF MECHANICAL ENGINEERING

PhD THESIS

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ABSTRACT

A methodological approach to process intensification (PI) has been developed to aid in the design of intensified chemical processes. Current process development procedures fail to consider if, and how, a chemical process can be intensified, resulting in limited application of PI in the chemicals industry. The PI methodology has been developed to meet these needs, focusing upon the chemical reaction stages of a process.

The PI methodology is a paper-based tool, based around a flowsheet known as the framework. Throughout development, the methodology was applied to industrial case studies which revealed considerations that should be included in the methodology and aided in determining its format. Each section of the framework contains checklists and procedures detailing the information required and the decisions to be made by the participants, who should be in a multi-disciplinary team. Examination of chemical reaction kinetics and the effects of mixing upon the reaction are key aspects of the methodology that are normally not examined during process development.

Incorporated within the methodology is a PI experimental protocol designed to model PI operation in the laboratory. Mixing theory was reviewed to identify that the protocol approach should be based upon recreating the mixing conditions experienced in a full scale plant within a small scale laboratory stirred vessel.

The developed laboratory protocol utilises semi-batch operation in a highly-mixed stirred vessel of 10cm diameter and height with twin pitched-blade turbine impellers. Turbulent energy dissipation rates of 150 W/kg can be achieved in the vessel. Experiments were run, showing that the performance of static mixer reactors can be predicted through the application of the protocol, though future work is required to develop this laboratory protocol approach into a rigorous experimental tool.

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This thesis is dedicated to my family for their continued support over the numerous years it has taken to get this far.

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NOTATION

a	feed pipe radius	m
A	reagent, 1-naphthol	-
B	reagent, diazotised sulfanilic acid	-
C	reagent, 2-naphthol	-
C_{i0}	initial concentration of species i	mol/m^3
C_i	final concentration of species i	mol/m^3
C_p	specific heat capacity	J/kgK
d	static mixer diameter	m
d_p	feed pipe diameter	m
D	impeller diameter	m
Da	Damköhler number	-
D_t	turbulent dispersion coefficient	m^2s^{-1}
D_{tr}	radial turbulent dispersion coefficient	m^2s^{-1}
E	reagent, aldehyde	-
E	rate of engulfment	s^{-1}
f_D	Darcy friction factor	-
fl	impeller flow number	-
F	reagent, aldehyde	-
G	reagent, aldol	-
H	reagent, diol	-
j	drop identifier	
k	turbulent kinetic energy	m^2s^2
k_i	second order reaction rate constant for species i	$m^3mol^{-1}s^{-1}$
L	turbulent macroscale	m
L_C	inertial convective disintegration lengthscale	m
L_D	lengthscale for initial dispersion of reaction the zone	m
m	mass of vessel contents	kg
M	mass flow rate	kgs^{-1}
N	impeller rotational speed	s^{-1}
n_f	number of feed pipes	-
P_O	impeller power number	-
Q	reagent, byproduct	-
Q	rate of heat release by reaction	W
Q_B	volumetric flow rate of additive through feedpipe	m^3s^{-1}
Q_i	volumetric flow rate through an impeller	m^3s^{-1}
R	reagent, desired product	-
Re	Reynolds number	-
R_i	rate of production or consumption of species i	$mols^{-1}$
S	reagent, byproduct	-
t	age of a reaction zone	s
t_{crit}	stirred vessel critical feed time	s
t_D	point source turbulent dispersion timescale	s
t_{Dl}	finite source turbulent dispersion timescale	s
t_{micro}	micromixing timescale	s

t_f	feed time into a semi-batch vessel	s
t_s	inertial convective disintegration timescale	s
T	reagent, intermediate product	-
T	dimensionless time	-
T	tank diameter	m
u	bulk liquid velocity in region of the feed pipe	ms^{-1}
$\bar{u}$	superficial liquid velocity	ms^{-1}
u_f	velocity of additive from feed pipe	ms^{-1}
u_t	impeller tip speed	ms^{-1}
V	volume	m^3
w	projected height of impeller blade	m
X_Q	yield of byproduct Q	-

GREEK SYMBOLS

α	flow ratio of bulk to additive stream	-
β	dilution factor for mass balance	-
β_{ij}	(rate constant of reaction)/(rate constant of slowest reaction)	-
γ	empirical correction factor	-
ΔT	temperature change	K
ϵ	specific turbulent energy dissipation rate	Wkg^{-1}
η	turbulence efficiency of a static mixer	-
θ	static mixer voidage	-
μ	dynamic viscosity	Nsm^{-1}
ν	kinematic viscosity (μ/ρ)	m^2s^{-1}
ρ	fluid density	kgm^{-1}

ABBREVIATIONS

KBS	Knowledge Based System
LDA	Laser Doppler Anemometry
LDV	Laser Doppler Velocimetry
MB	Mass Balance
PBT	Pitched Blade Turbine
PI	Process Intensification
STR	Stirred Tank Reactor

CHAPTER 1
INTRODUCTION

1.1 BACKGROUND

The chemicals industry employs a range of processing technology to manufacture its products. The stirred tank reactor in particular is used in processes accounting for more than half of the value of world's chemical production (Butcher and McGrath, 1993). Stirred tank reactors are known to provide sub-optimal performance for many processes, with inefficiencies resulting from inadequate mass and heat transfer, restricting the rate of production. These inefficiencies are tolerated due to the versatility of the equipment and wide confidence in its operation.

Increasingly, the examination of other production methods is becoming desirable to reduce capital and operating costs as well as to meet environmental and safety requirements. The move to different production methods requires a step change in the processing technology used, rather than incremental improvements of the existing technology (Akay *et al*, 1997). This is achieved by designing plant to meet the needs of the process, rather than fitting the process into standard plant, resulting in plant equipment that is smaller, safer and cheaper.

The application of new, smaller plant equipment is known as process intensification (PI). The term first arose in the late 1970s to describe a means of reducing the capital cost of large chemical manufacturing facilities (Ramshaw, 1985), with safety and operability considerations having become important drivers towards PI. Most unit operations on a plant can be intensified, but the chemical reactor is where most benefits are to be gained as any improvements made here affect the entire plant (Hannon, 1992).

Chemical reactor PI requires that reactants are fully mixed together in a timescale shorter than that of the reaction. Providing any heat of reaction can be extracted, all

mechanical rate limiting features are removed and the reaction progresses at its inherent kinetic rate. By operating in a continuous manner, reactor residence times can be matched to the reaction time and, if the reaction kinetics are fast, very small reactors can result.

Smaller reactors reduce the inventory of reacting materials present at any time. Coupled with the design of the reactor reducing the potential for dangerous operating conditions to be reached, process safety is greatly improved. Making safety intrinsic to the design of the equipment in this manner is known as inherent safety (Kletz, 1998a), a subject which is examined and appreciated in industry. A wide range of technology is available for reactor intensification, including static mixers which are pipe inserts that promote rapid mixing in continuous flow operations.

PI is becoming recognised as a factor that will play an important role in the future of the chemicals industry. Despite the many benefits that PI can deliver, application is limited. Process development procedures play a large part in the limited application of PI. Process development in the fine/speciality chemicals sector is based on batch or semi-batchwise operation at the laboratory scale which is then scaled up to large stirred vessels. Bulk chemical production facilities are normally operated continuously for economic reasons, but again standard equipment is preferred. A root cause of the limited application of PI is the lack of procedures for determining if and how a process can be intensified (Borland, 1996, and Kletz, 1998b). Such procedures are needed to encourage the consideration of PI throughout process development and demonstrate the benefits of its operation. This would then work towards removing other significant barriers to PI, in particular conservatism and lack of awareness of what it can achieve.

To apply PI, new process development procedures will have to change the mind-set of using only standard technology and promote consideration of other means of operating by identifying the potential for intensification at the earliest possible stage. A number of methodologies concerning process development have been published, particularly relating to inherently safe operation (e.g. Mansfield, 1996). References to PI within

these are limited, despite it being a key means of achieving inherent safety. The major areas that require addressing for PI to be properly considered are firstly determining whether a chemical process can be intensified, and secondly setting out the procedures for design of an intensified plant.

Potential for intensification can be determined in some cases through examination of the mixing effects on a chemical reaction scheme. Rapid mixing benefits faster reactions, but mixing characteristics tend not to be examined, meaning PI operation is overlooked (Industrial Communication, see Appendix A). Even if mixing is examined, the intensity of mixing achievable in laboratory vessels is far lower than that experienced within PI equipment and therefore the full benefits of PI operation cannot be evaluated. In addition, there is no ability to model continuous operation in normal laboratory equipment, resulting in this option not being fully examined.

This work is concerned with the development of a methodology for redefining the approach to process development to encourage the consideration of PI. Experimental techniques for proving the performance and benefits of PI operation are incorporated within the overall methodology structure. Such procedures are essential for increasing the uptake of PI and realising the benefits that it can provide.

1.2 LAYOUT OF THIS THESIS

Chapter 2 introduces the concept and definitions of PI. Mixing theory explains how PI achieves its benefits, with some PI equipment described to show how smaller, safer and cheaper plants are realised. Reasons for lack of consideration of PI within existing process development procedures are explained and other barriers preventing applications of PI are covered.

Existing process development methodologies are reviewed in Chapter 3, illustrating the lack of PI references within these. The approaches taken by the published

methodologies are considered as the means of operating a PI methodology.

Chapter 4 covers development of the PI methodology. It begins with the ideal procedures that should be followed to achieve a PI plant and turns these into a usable tool through the aid of industrial case studies. The requirements for each methodological stage are identified and discussed.

Laboratory protocol experiments to model PI operation are an integral part of the PI methodology. Procedures for this laboratory protocol are developed in Chapter 5, resulting in the design of the protocol equipment and experimental testing that show how continuous PI operation can be simulated in a semi-batch laboratory scale stirred vessel.

Chapter 6 is a full description of the developed PI methodology, including the procedures by which it should be followed.

Chapter 7 discusses the PI methodology and draws conclusions from this thesis. Areas that will benefit from further development are identified.

CHAPTER 2

PROCESS INTENSIFICATION IN THE CHEMICALS INDUSTRY

2.1 INTRODUCTION

Process Intensification (PI) is an approach to making a significant reduction in the size of a chemical plant by designing it to meet the needs of the process. Size reduction decreases capital and operating costs and improves safety by reducing the inventory of the plant. The concept of PI has been around since the late 1970s, but it is only now gaining wider acceptance in the chemicals industry.

The development of the definition and objectives of PI is described in this chapter, showing how it is becoming perceived as the desirable approach to plant design and operation. Examples of PI equipment and a review of mixing theory demonstrate how PI achieves its benefits by applying technology that meets the needs of the chemical process. A review of current chemical process development procedures identifies the sectors of the chemicals industry where the potential for PI is the highest and highlights the drivers towards and against implementation of novel technology.

2.2 DEFINITIONS OF PROCESS INTENSIFICATION

The term PI was introduced in the late 1970s as a means of reducing the capital cost of large chemical plants. Ramshaw (1985) recognised that much of a plant capital cost was related to the civil engineering structure, which could be between two and seven times the capital cost of the individual plant items. Significant savings can therefore be made if the chemical plant is much smaller, preferably by orders of magnitude. Wakeman and Akay (1996) support this view by stating the primary incentive for PI is to reduce the cost of a plant by reducing the size of equipment needed to achieve a given production objective.

The size reduction that should result from PI is not agreed. Akay *et al* (1997) state "..it is generally accepted that it should be at least tenfold and preferably much more". According to Ramshaw (1995), "Volume reductions in the order of greater than 100 must be our target". Pilavachi (1993) says "PI may be defined as the use of methods or equipment which will reduce the plant size by a factor of at least three for a given throughput", whilst Mercer (1993), reports that it is "..the established convention within the industry that PI relates to reductions of at least 3-4 fold in magnitude" to achieve the same level of manufacturing output. Despite the variations on the scale of reduction required for a process to be deemed intensified, all sources are in agreement that significant size, and hence operating and capital cost, reductions must be achieved for PI to have a major impact.

Process safety soon became a significant additional driver for PI. An explosion at Flixborough in 1974 killed 28 people and started the systematic study of plant hazards and safety to design safer plants. Kletz (1998a) describes the progress of plant safety design arising from the Flixborough accident to the current position, where the preferred approach is not to add safety equipment to a near-finalised plant, but to design a plant that is less likely to go wrong in the first place. This concept is known as inherent safety. A favoured approach to inherent safety is intensification to reduce plant inventory.

PI is achieved by improving the performance of plant unit operations to obtain a given performance in much smaller equipment. Akay *et al* (1997) state that this performance improvement requires a step change in both thinking and technology, rather than incremental improvements in existing technology. Applied to chemical reactors, this new technology would "provide a fluid dynamic environment within each reactor, so that performance is dictated by intrinsic chemical kinetics rather than heat transfer or mass transfer restrictions".

Removing physical restrictions in a plant means that reactions can run to completion in a shorter timescale. This is achieved by providing extended surface area for mass

transfer, heat transfer and reaction. PI is best applied to continuous operation where the residence time can be tailored to match the reaction kinetics. Fast reaction kinetics benefit most from PI as the short timescale needed for a fast reaction to run to completion results in very small equipment.

The chemical reactor has been described by Hannon (1992) as the nucleus of the chemical plant. Performance of the reactor dictates the design of the rest of the plant and any improvements made to the reactor will provide the widest ranging benefits. Therefore the reactor is where consideration of PI should be focused.

Other sources also emphasise the need for changing the procedures by which new chemical processes are developed to allow new technologies to be applied. One such view is given by Green (1998) who says PI is "a novel design approach where fundamental process needs and business considerations are analysed and innovative process technologies used to meet these optimally ". The fundamental process needs are, for example, mass transfer requirements. The reference to business considerations recognises that often the main driver for intensification is to improve economics of the process, whether in capital and operating costs, or by achieving safety in the most cost-effective manner. Other business considerations include the need to maintain a competitive edge. With the European chemicals industry under threat from cheaper manufacturing in the East (Nightingale, 1996), firms have to find means of reducing costs. One such means is to utilise the new technologies and procedures that PI can deliver.

PI benefits have been demonstrated on the production of Caro's Acid (Whiting, 1992). The traditional manufacturing method required bulky and expensive refrigeration equipment to produce 300kg/day from a 30 litre stirred vessel. The new plant comprises a small, continuous, adiabatically operating tubular reactor. Residence time is less than a second with up to 1000kg/day made on demand from a volume of only 20ml. Major benefits include lower production costs and the ability to manufacture on-site without the need for hazardous storage or transportation.

2.3 THE CHEMICALS INDUSTRY

The chemicals industry can be considered as consisting of two main sectors: high volume production bulk chemicals and low volume production fine/speciality chemicals (Heaton, 1994). Bulk chemicals, for example petrochemicals, are produced on the scale of tens to hundreds of thousands of tonnes per annum, with plants dedicated to a single product and operating in a continuous manner. Fine/speciality chemicals include pharmaceuticals and dyes and have a low throughput of tens to a few thousand tonnes per annum. There are a large number of small producers who operate batch or semi-batchwise in multi-product plants. Batch operation is where the reactants are charged to the vessel and left until reaction is complete, whereas semi-batch is where one reactant is charged to the vessel and another added over a period of time.

The means of production is distinctly batch for fine/speciality chemicals and continuous for bulk chemicals for a number of reasons, which are discussed by Sharratt (1996). The advantages of continuous processing become more significant on increasing scale, with the primary advantage being reduced size compared to a batch plant of the same production capability. This in turn reduces capital cost, working capital and hold-up of materials. Thermal integration, where heat is re-used in the same process, is possible, allowing substantial energy savings which is very important in the low profit margin manufacturing of bulk chemicals. Fine/speciality chemical companies tend to manufacture small volumes of a large number of products, so require highly versatile production facilities which continuous processing cannot provide. Batch production also requires less development time, with less complex control and operating systems, although manpower requirements are increased (Coulson and Richardson, 1994).

Stirred tank reactors (STRs) are widely employed on both fine/speciality and bulk chemical production plants due to their versatility in manufacturing a wide range of products and handling different process conditions. The STR consists of an upright cylindrical vessel with a volume of up to tens of thousands of litres, mixed by an impeller that is selected according to the required duty. STRs can be used either

batchwise or continuously as a single vessel or a series of tanks. Butcher and McGrath (1993) state that more than 50% of the value of the world's chemical production involves the use of STRs, making it a very important and widely recognised plant item. Plug flow reactors (PFRs) are also common for continuous processing. Woods (1995) describes the general PFRs that are available, which include tubular reactors, bubble columns, thin film reactors and transported bed or slurry reactors.

A consequence of the STR being so versatile is that it is sub-optimal for many of the processes it operates. The variability in local mixing uniformity throughout the vessel, which according to Butcher and McGrath (1993), is typically 50:1 between different regions, can have an impact upon productivity and safety. Poor mixing can cause high localised concentrations of a fed component additive and high localised temperatures which, coupled with long residence times, can increase by-product formation. Fasano and Penney (1991) and Kenat (1999) discuss this problem in more detail. Mixing in STRs can be improved through the use of multiple impellers which distribute the mixing intensity more evenly throughout the vessel volume. Lee and Yianneskis (1997) state that two impellers give more rigorous mixing and the time taken to reach a fully mixed state is less than for a single impeller system, though power consumption is increased.

Heat transfer from STRs is relatively poor due to the low heat transfer surface area to vessel volume ratio. Restricted heat transfer has been a major cause of chemical accidents, as documented by Barton and Nolan (1989) who noted 189 thermal runaway incidents over a period of 25 years. Thermal runaway occurs when the heat generated by reactions exceeds the heat removal capabilities of the equipment, speeding up the reaction and rate of heat release until the reaction becomes uncontrollable. To prevent this scenario, feed is often added slowly to allow the equipment to handle the heat removal, which increases the production timescale.

The problems associated with the STR led Villermaux (1993) to question whether it would be preferable to develop simpler and more efficient mixing systems rather than

persevering with the STR, a view that is shared by plant operators (Industrial Communication, see Appendix A). The more efficient mixing systems could include PI technologies.

2.4 PROCESS INTENSIFICATION TECHNOLOGIES

A wide range of PI technologies exists for replacing many of the unit operations found on a chemical plant. Some of these technologies are overviewed here, most of which are introduced by Green (1998) and Akay *et al* (1997). Three major groups of PI equipment can be identified: in-line mixing; extended heat transfer area; intensified force fields. All of these operate by increasing the mixing and/or heat transfer rates compared to conventional equipment.

In-line mixing involves continuously mixing fluids in a pipeline. The simplest form of in-line mixer is a tee-mixer, where a liquid jet from a side pipe joins the bulk flow in the main pipe, rapidly mixing the two streams. More intensive mixing for blending and reacting duties can be provided by static mixers, which are pipeline inserts designed to promote mixing. Various static mixer designs are available for different blending duties, depending upon factors such as the phase and viscosity of the system. Three static mixer types are illustrated in Figure 2.1. Static mixers find applications in single phase liquid, gas/liquid and liquid/liquid systems. Operability considerations of static mixers have been described by Streiff and Rogers (1994) and Myers *et al* (1997). Benefits of static mixers include: homogenous mixing; narrow residence time distribution; low cost and low maintenance due to lack of moving parts. Limitations include: handling of very viscous materials or solids which could block the mixers; poor flexibility for providing a range of process conditions; poor turndown where flow rate cannot be reduced without significantly affecting the mixing conditions.

Gas/liquid mixing can be intensified by the use of ejectors. The liquid phase is pumped through a nozzle, entraining and mixing gas from the surroundings. Far higher inter-

phase contact and mass transfer rates can be achieved than in a conventional bubble column or sparged stirred tank. Two-phase liquid systems, for example emulsions, can be rapidly blended by rotor-stator mixers. A fixed stator is positioned around a rapidly moving rotor, providing very high shear and mixing rates in the region around the unit. Ordinary liquid pumps can also be used for in-line blending, though mixing is limited. An example has been noted where the need for a stirred vessel was removed simply by adding the stream to be blended into an existing pump (Industrial Communication, see Appendix A).

Heat exchange intensification is achieved by using compact heat exchangers which provide a higher amount of heat transfer surface area per unit volume of heat exchanger, reducing the required unit size. According to Mercer (1993), a compact heat exchanger is one with heat transfer area per unit volume in excess of $700m^2/m^3$, compared to a value of $100m^2/m^3$ typically experienced within shell and tube heat exchangers. Different types of compact heat exchangers are described by Johnston (1986), with plate and frame heat exchangers being widely used. The small channels in compact heat exchangers can block easily, but fouling is limited by the higher shear experienced within the unit.

Combining reaction and heat exchange into a single unit can allow fast, exothermic reactions to run isothermally. Benefits of this approach are shown by Edge *et al* (1997) who predict a 50% reduction in by-product formation for an industrial reaction scheme. Reactor heat exchangers can be based upon plate and frame, or shell and tube with static mixer inserts to aid mixing.

Burns and Ramshaw (1999) describe a microreactor that combines reaction with heat exchange. Heat transfer coefficients are improved through the use of a large heat transfer surface area to unit volume ratio, and small heat transfer distances. A bore size of 127μm in a simple capillary tube could achieve rapid reaction with a production rate of 0.1μl/s, or 0.36l/h. Microchannel reactors could be stacked in blocks of hundreds or thousands of channels to increase the production rate. Microreactor technology is

receiving interest in the chemicals industry, though no commercial production is yet using the technology. One drawback is that even when scaled up through the use of multiple channels, the production rate is too low for many commercial processes

Externally sourced force fields can be applied to a system, increasing inter-phase surface area for mass and heat transfer. One such approach is centrifugal field operation. This has been extensively studied by Ramshaw (1993) who developed the Higee unit. Higee consists of a rotating matrix of fine filaments within which the dense phase moves outwards against an inward flow of the light phase. Uses include being an alternative to distillation columns. The Chinese are investing heavily in Higee technology with applications made in water deaerating (Zheng *et al*, 1997). The Spinning Disk Reactor also utilises centrifugal forces (Boodhoo *et al*, 1997). Reacting fluid flows over the surface of rotating discs in thin, wavy films which have high mass and heat transfer coefficients. Initial costs of centrifugal devices are high, but the small support structure required can reduce the overall capital outlay, with additional advantages of low inventory and short residence time.

2.5 MIXING THEORY LITERATURE REVIEW

Mixing is the mechanism that brings reactants together on the molecular scale so that the reaction can occur, and is an area where many of the PI equipment types described above achieve their benefits. Mixing intensification is hence examined further to show how improving mixing benefits reactions, allowing them to be intensified. Procedures for determining the mixing rates within both stirred tanks and static mixers, which are among the more versatile pieces of PI equipment, are covered as these play a key role in the subsequent development of the PI methodology in this work.

2.5.1 Mixing Scales and Turbulent Energy Dissipation

Three major scales of mixing can be identified (Baldyga and Pohorecki, 1995):

Macromixing	Large scale blending of an additive throughout a vessel
Mesomixing	Mixing of an additive with its local surroundings
Micromixing	Molecular level mixing to allow reaction

The rate of mixing at each scale depends upon the mixing power input into the system, with higher power input increasing the rate of mixing. The mixing power input is expressed as the turbulent energy dissipation rate, ϵ, with units of watts of energy dissipated per kilogram of inventory (W/kg). Static mixers produce 1-1000 W/kg with good mixing homogeneity throughout the mixer volume, with Hearn (1995) finding only a 4-fold variation in ϵ across a single element of a Kenics static mixer. In comparison Butcher and McGrath (1993) state that ϵ in stirred vessels is around 1-10 W/kg, with variations typically 50:1. This variation can be much greater, as shown by Bourne *et al* (1992) who investigated a 2.5 litre stirred vessel where ϵ was 180 W/kg in the impeller region, but only 1W/kg nearer the surface.

Average turbulent energy dissipation rate is easily determined as the power input divided by mass of contents. Coulson and Richardson (1990) show how the power input for a stirred vessel is derived, which forms the top right-hand side of Equation 2.1 below.

$$\epsilon = \frac{P_0 \rho N^3 D^5}{m} \qquad (2.1)$$

Approximate values for P_0, the impeller power number, are: 5 for Rushton turbines; 1.3 for pitched blade turbines; 1 for propellers. ρ is the fluid density. N and D are the impeller speed and diameter respectively and m the mass of the vessel contents.

Mixing energy in static mixers results from pressure drop being converted into turbulence. Each type of static mixer converts a different proportion of the total turbulence into mixing energy, known as the turbulence efficiency, η. For static mixers, the turbulent energy dissipation rate is given by Hearn (1995):

$$\epsilon = \eta \left(\frac{f_D \, \bar{u}^3}{2 \, d \, \theta} \right) \qquad (2.2)$$

Superficial fluid velocity, $\bar{u}$, is obtained by dividing the volumetric flow rate through the mixer by the cross-sectional area, with d being the static mixer diameter. Turbulence efficiency, η, Darcy friction factor, f_D, and mixer voidage θ vary between different types of static mixer. Values for these variables have been determined by Hearn (1995) and shown in Table 2.1, with the efficiency values stated to be ±10%.

Table 2.1 Variable values for some static mixers

Mixer type	voidage	efficiency, η	friction factor, f_D
HEV	0.99	80%	0.43
Kenics	0.90	60%	1.9
SMXL	0.90	70%	2.6

2.5.2 Mixing Timescale Correlations

The objective of chemical reactor intensification is to allow a reaction to run at its inherent kinetic rate by mixing faster than the reaction timescale. To achieve this, it is necessary to be able to determine the mixing timescales within a reactor so these can be compared to the kinetics. Mesomixing and micromixing are the most relevant mechanisms to reactive mixing with fast kinetics where one reactant is added to another in a controlled manner. Correlations and mixing models that enable estimation of meso- and micromixing timescales for both stirred vessels and static mixers are described below.

Mesomixing describes the breaking down of an additive stream from a feed pipe into the surroundings. It is larger in scale than micromixing that brings molecules together for reaction, but is on a far smaller scale than macromixing, which relates to blending

throughout the vessel. Two different mesomixing mechanisms are described by Baldyga *et al* (1997):

a) Turbulent dispersion of a feed stream

b) Inertial convective disintegration of large eddies in the course of dispersion

a) Turbulent Dispersion Mesomixing

In turbulent dispersion, the feed stream spreads out transverse to its local streamline. This mechanism is also used to describe macromixing in static mixers where the radial mixing action rapidly fills the entire cross-sectional area with additive. Two scenarios for turbulent dispersion are: point source, where L_D, the characteristic length scale for initial dispersion of the reaction zone, is much smaller than the feed pipe diameter; finite source, where L_D is equivalent to, or greater than, the feed pipe diameter. Both of these approaches are derived and discussed by Baldyga and Pohorecki (1995).

Baldyga and Bourne (1992) give the following correlation for L_D:

$$L_D = \left(\frac{Q_B}{u} \right)^{\frac{1}{2}} \qquad (2.3)$$

Q_B is the volumetric flow rate of additive. For stirred vessels, local flow velocity, u, was found to be approximately 25% of the impeller tip speed for a Rushton turbine by McCabe (1985), obtained through the use of small velocity probes and photographic measurements of tracer particles. The value of 25% for a Rushton turbine is also used by Baldyga, Bourne and Yang Yang (1993). A non-intrusive technique is available for velocity measurements in the form of Laser Doppler Velocimetry (LDV), also known as Laser Doppler Anemometry (LDA). A laser is used to examine the flow pattern and allows determination of the velocity vectors. Mavros and Baudou (1997) used LDV with a 6-blade turbine and found that the global mean velocity is approximately 18% of the tip speed. No information was found for other impeller types.

Point source turbulent dispersion timescale, t_D, is given by

$$t_D = \frac{Q_B}{n_f\, u\, D_t} \tag{2.4}$$

where n_f is the number of feed pipes used for addition and D_t the turbulent dispersion coefficient. D_t is related to turbulent kinetic energy, k and its dissipation rate, ϵ, by

$$D_t = \frac{0.1\, k^2}{\epsilon} \tag{2.5}$$

where

$$\epsilon = \frac{0.85\, k^{3/2}}{L} \tag{2.6}$$

L is a measure of the turbulent macroscale and has been identified as 0.52w by Baldyga and Bourne (1992) where w is the height or projected height of the impeller blade. Using Equations 2.6 and 2.5 to substitute for D_t in Equation 2.4 gives:

$$t_D = \frac{Q_B}{0.124\; n_f\, u\; \epsilon^{1/3}\; L^{4/3}} \tag{2.7}$$

Finite source turbulent dispersion timescale, t_{D1}, is determined from:

$$t_{D1} = \frac{a^2}{D_t} \tag{2.8}$$

where a is the feed pipe radius. Substituting for D_t using Equations 2.5 and 2.6 leads to:

$$t_{D1} = \frac{a^2}{0.124\, \epsilon^{1/3} L^{4/3} n_f} \tag{2.9}$$

Static mixer turbulent dispersion timescale correlations are similar to Equations 2.4 and 2.8 above, with D_t replaced by D_r, the radial turbulent dispersion coefficient. Hearn

(1995), experimentally obtained values of D_{tr} through the use of LDA, with typical values of D_{tr} being of the order of 10^{-4} m^2s^{-1}.

b) Inertial Convective Disintegration Mesomixing

This mechanism describes how large eddies of additive disintegrate in the course of dispersion and reduce by inertial action towards the micromixing scale. Baldyga *et al* (1997), give the following correlation for the inertial convective disintegration mesomixing timescale, t_S.

$$t_S = 2\left(\frac{L_c^2}{\epsilon}\right)^{1/3} \qquad (2.10)$$

Possible means of estimating L_C, the integral length scale of inertial convective disintegration, include comparison to the feed pipe diameter, though this is stated to lack experimental verification by Baldyga *et al* (1997). A continuity equation based on feed entering a uniform mixer flow has been developed by Baldyga *et al* (1995). This is very similar to Equation 2.3 for determining L_D, and can be represented as:

$$L_C^2 = \frac{4Q_B}{\pi\, u\, n_f} \qquad (2.11)$$

Substituting for L_C^2 in Equation 2.10 gives

$$t_S = 2.17\left(\frac{Q_B}{u\,\epsilon\,n_f}\right)^{1/3} \qquad (2.12)$$

Estimating the characteristic length scale for both turbulent dispersion and inertial convective disintegration is the aspect which currently limits confidence in the results of the above mesomixing correlations. As a result, according to Baldyga *et al* (1997) "The approaches towards estimating mesomixing length and time scales should be regarded as tentative".

Micromixing

Micromixing refers to mixing on the molecular scale where chemical reaction takes place. The engulfment model of micromixing, which relates to mutual engulfment of regions having different compositions, is described by Baldyga and Bourne (1989). A resulting correlation which can be applied to both stirred tank and static mixer operation is given by Hearn (1995). ν is the kinematic viscosity of the system.

$$t_{micro} = 17.2 \left(\frac{\nu}{\epsilon} \right)^{1/2} \qquad (2.13)$$

2.5.3 Mixing-Sensitive Reactions

When the rate of mixing is not faster than the chemical reaction rate, changing the rate of mixing can affect the product quality of competitive reaction schemes. This is known as mixing-sensitivity, and is used to illustrate how PI achieves some of its benefits.

The azo-coupling reaction scheme is a competitive parallel and consecutive reaction scheme that has been used to characterise mixing within intensified and conventional reactors (Bourne *et al*, 1992). Full details of the scheme and experimental procedures are contained in Appendix B, with an outline of the reactions given below.

$$\underset{\text{desired reaction}}{A + B \xrightarrow{k_1} R} \qquad \underset{\text{consecutive}}{R + B \xrightarrow{k_2} S} \qquad \underset{\text{parallel}}{C + B \xrightarrow{k_3} Q} \qquad k_1 > k_2 > k_3 \qquad (2.14)$$

A and C are 1- and 2-naphthol respectively. B is diazotised sulfanilic acid. Product R is defined as the desired product and is formed by the fastest reaction, with k being the reaction rate constant for each reaction step. S and Q are akin to by-products, with yield of by-product Q, X_Q, used to characterise the mixing performance within the system. If mixing is faster than all of the reactions, the process becomes kinetically limited and X_Q minimised. The product yields are determined through spectrophotometry, from

which the turbulent energy dissipation rate within the system at the time of reaction can be determined.

Reactant B is added to bulk solution containing both A and C. In semi-batch operation, this addition occurs over a period of time, t_f, with the reaction taking place in a volume known as the reaction zone. Slow feeding, or low feed flow rate Q_B, results in very small B-rich zones that rapidly mesomix with the surrounding fluid, leaving micromixing as the limiting mechanism. This is known as micromixing control, and produces the minimum amount of by-product formation. Increasing the feed rate results in larger B-rich zones that require longer to mesomix than micromix, resulting in mesomixing control. This increases the length of time reactant B is in contact with C and R in the reaction zone, and hence increases the by-product production. Increasing the turbulent energy dissipation rate decreases both the meso- and micromixing timescales and improves dispersion of B throughout the vessel volume, reducing the by-product formation for a given feed time.

As the feed time is increased, by-product yield reduces to an asymptote where the reaction becomes micromixing controlled. The point where this asymptote begins is known as the critical feed time, t_{crit}. Figure 2.2 illustrates this effect.

The critical feed time is the ideal operating point for semi-batch STRs as, according to Bourne and Thoma (1991), this generates the maximum productivity with constant product quality. Critical feed time can be as long as several hours in large vessels. Increasing the impeller speed N, and hence the turbulent energy dissipation rate ϵ, shifts the curve downwards and towards the origin. This reduces the critical feed time, as shown experimentally by Bourne and Thoma (1991) where critical feed time for a 19 litre vessel was 500 seconds at 76 rpm, 250 seconds at 156 rpm and 180 seconds at 227rpm. Critical feed time was determined through inspection of experimental results.

Continuous operation in static mixers can be considered to be the equivalent of a very short feed addition time in Figure 2.2, as all the feed is added stoichiometrically, but

takes a short period of time to be fully blended across the static mixer cross-section. Mesomixing control would be expected to occur in static mixers due to this very short additive timescale. This has been shown to occur by Baldyga *et al* (1997), though does depend heavily upon the flow conditions in each particular case, with micromixing control tending to occur at lower bulk flow rates and mesomixing control at higher bulk flow rates.

Static mixer operation is subject to self-engulfment (Baldyga & Bourne, 1999, Chapter 8). Self-engulfment occurs if the local volume fraction of additive is not vanishingly small, and additive-rich volumes mix with each other rather than the bulk additive. This increases by-product production. Self-engulfment occurs in static mixers as the reaction zone rapidly fills the entire cross-sectional area of the static mixer and cannot expand further, so mixes in with itself. This will not occur in semi-batch stirred tank operation. By-product yield increases due to self-engulfment in static mixers but it can be compensated for through the use of higher turbulent energy dissipation rates, although at the expense of increased pressure drop and therefore increased energy usage.

2.5.4 Mixing Summary

The effects of mixing on competitive reactions demonstrates how PI can provide many benefits. Increasing mixing rates changes a reaction from being mixing limited to kinetically limited. Once kinetic control is achieved, yield of by-products reaches a minimum value and there will be no benefit in increasing the mixing rate further. Mixing occurs on different scales within a system. The time- scale for each mixing mechanism can be estimated, giving an indication of the controlling mixing mechanism. This can then be matched to the reaction kinetics. Faster reactions will benefit most from the rapid mixing provided by PI equipment, but for slower reactions the rate of mixing provided by conventional reactors will be sufficient to meet the needs of the chemistry.

2.6 CHEMICAL PROCESS DEVELOPMENT

PI is not widely applied, despite being able to significantly improve process performance through improved mass and heat transfer capabilities. Current process development procedures are now reviewed to show the difficulties that have to be overcome to allow PI to be increasingly considered and applied.

2.6.1 Chemical Synthesis Route Selection

Process development commences with chemists generating a number of synthesis routes to manufacture a target product. Screening of synthesis routes takes place to select the most appropriate one. A number of factors can influence the choice of route, from availability of raw materials right through to eventual disposal of wastes, as described by Lee and Robinson (1995). At this stage of development, the likely process plant has to be considered to allow a preliminary assessment of production costs, aiding in the selection of the synthesis route. Many fine/speciality processes are developed to operate batch or semi-batchwise in standard STRs. As a result, alternative technologies do not get considered. This automatic assumption of operation in STRs is a plant-constrained approach, with a view being aired from more than one source that chemists may inhibit faster reactions to ensure they are more controllable when operating in STRs (Industrial Communication, see Appendix A). According to Borland (1997) the opportunity for using any innovative technology at this stage is lost simply because it is not considered.

Experiments are run on the chosen synthesis route to determine optimum operating conditions. The process variables normally experimented with are: stoichiometry; concentration; temperature; rate of addition; residence time (Industrial Communication, see Appendix A). These experiments form a potential barrier to the application of PI, as the tendency to use only versatile STRs leads to the chemistry and reaction procedures being developed around batch and semi-batch procedures. Crucially, mixing effects and the fluid dynamic environment tend not to be examined even though

it has been shown in Section 2.5.3 that this can play a significant part in the process performance.

Often the kinetics of a reaction scheme are not known or examined. Lack of kinetic information can mean that it is never clear whether the reaction is slow and really takes several minutes or hours to go to completion, or whether the kinetics are fast and the reaction rate is limited by the equipment in which the process is run. Fasano and Penney (1991) state that kinetics may be impossible to determine accurately, though for the purposes of process development even an appreciation of the reaction rate would be of benefit.

Thermodynamics of a reaction scheme are normally examined as this involves important safety considerations. Conditions that initiate runaway reactions in STRs should be evaluated and avoided on the plant, with Gygax (1990) giving some procedures by which this may be achieved. Calorimetry, where the heat generation is measured under controlled conditions, is the usual approach for determining thermodynamics, as described by Singh (1993). Kinetics of a reaction can be evaluated through calorimetry by observing the rate of temperature rise in a reaction mixture, as shown by Crevatin *et al* (1999) for a ketonization reaction.

2.6.2 Chemist and Chemical Engineer Interface

At some stage in process development, the project is handed over from development chemists to chemical engineers. According to Yates (1996), the contribution of the chemist is to identify the combinations of chemistry, catalyst and conditions which lead to optimal conversions to the desired product. Consequently the chemical engineer's contribution is to identify practical, economic and safe equipment configurations which allow these circumstances to be achieved. In smaller companies, the chemist can control process development right up until the point where it has to be scaled-up into the full scale plant, by which time the manufacturing equipment has already been selected (Industrial communication, see Appendix A). In others companies, chemical

engineers may get involved earlier by examining the engineering feasibility of the synthesis route options.

Douglas (1988) provides lists of the information required from chemists to enable the design of chemical processes, reproduced in Figure 2.3. It is stated that the information that is often available includes the primary reactions, temperature and pressure ranges, the catalyst and the maximum yield. Other required information relates to the costs of raw materials, allowing for an economic evaluation of the process. For any information that is not available, Douglas suggests that it is essential to work closely with a chemist to gather remaining data.

Other sources have identified the need for chemists and engineers to work together during process development. Yates (1996) states that chemists and engineers approach process development from different perspectives and have different views on what is important. For process development to be successful, they must work together and have an understanding of, and respect for, each others contribution. Experience has been reported of chemists preferring to seek different synthesis routes for unsafe reactions rather than allowing engineers to apply a cheaper engineering solution (Industrial Communication, see Appendix A). If chemists and engineers worked together, the engineers could ask the right questions about kinetics and chemists supply the required information, allowing the plant to be designed to meet the needs of the process. Multi-disciplinary teams are now beginning to be employed to improve process development procedures (Industrial Communication, see Appendix A).

Projects for developing second generation plant are included within process development. A second generation plant is one where the process has been operating for a number of years, but a new plant is required to improve safety or reduce costs. Under these circumstances the chemical synthesis route is set, but there may still be the opportunity to improve the process, for example through the use of different catalysts or reagents. Even in processes run for a number of years, it has been found that the kinetics of the reactions are rarely known (Industrial Communication, see Appendix A)

which mirrors the difficulty in obtaining kinetics for new processes. Many of the other issues above relating to determination of ideal operating conditions and interaction between chemists and engineers will still apply. Plant operators may be able to play an important role in the procedures as they have experience of the plant operation, so may be able to suggest potential means for improving performance.

2.6.3 Scale-up

The final stage of process development is scale-up to the production plant. Scale-up involves translating small scale results to the large scale to make more material per unit time, possibly increasing plant size by several orders of magnitude. Plants tend to be designed for volume first and performance second, with Trambouze (1990) saying that scale-up is normally a compromise between technical performance and economics. The volume approach to scale-up does not apply to PI where the full scale plant may be of a similar size to the laboratory scale, but the principle of making more material per unit time is still relevant.

Often problems can occur during large volume scale-up as laboratory experiments provide far more intensive conditions than those achieved by a full scale conventional plant. This is particularly true for heat and mass transfer capabilities which decrease as a stirred tank size increases, meaning product quality can suffer and processing times increase significantly between laboratory and large scale operation.

An increased understanding of the process has been identified as a means of minimising problems on scale-up. Leng (1991) approaches this by setting out procedures to define the process needs, select the important process parameters, and then choose an equipment design to match these parameters. Muller (1996) developed a computer model to aid the transfer from laboratory to full scale production. This requires a description of the chemistry and process requirements, for example key reaction mechanisms and mass transfer requirements, some of which may require experimentation. It is claimed that the modelling focuses laboratory experimentation,

providing a tool which can eliminate the need for pilot scale trials.

Trambouze (1990) identifies that scale-up should not create problems if development experiments were "..designed to simulate the industrial reactor. In other words, the real problems often lie in scale down, rather than scale-up.". This approach requires laboratory equipment whose performance matches that of the full scale. This view is reflected by Yates (1996) who suggests that any changes in conditions in scale-up should be anticipated and experiments run with these differences in mind. However, Yates also illustrates the previously noted lack of consideration of mixing effects as his discussion on scale-up problems focuses only on heat transfer limitations. Kenat (1999) discusses designing pilot plant specifically to obtain information that laboratory scale operation cannot produce, and therefore minimising scale-up difficulties.

The approach of designing the laboratory equipment to match the performance of the full scale plant is equally applicable to PI operations. To achieve a fluid dynamic environment that allows the reaction to run at its inherent kinetic rate, very rapid mixing and heat transfer may be required. However, the very same laboratory experiments that provide mass and heat transfer rates too high for conventional scale-up cannot provide rates high enough to model PI operations.

2.6.4 Summary of Process Development Procedures

Changes are required in process development and scale-up to allow the full consideration and application of PI. The current practice of developing the chemistry to operate in STRs restricts the potential for engineers to then examine the feasibility for intensification through the use of continuous processes. More focused laboratory experiments are required to provide the necessary information to determine the benefits that PI operation can bring to a process.

2.7 PROCESS INTENSIFICATION EXPERIMENTAL PROCEDURES

A key aspect identified above for improving process development procedures is to improve the link between the laboratory and plant operation by running experiments under the same conditions that will be experienced on the full scale plant. This will then minimise unexpected problems arising on scale-up and provide a better insight into the operation of a full scale plant, whether conventional or intensified. Some experimental procedures have been suggested for modelling PI operations and are discussed below.

Chemical kinetics are often not determined, though it is necessary to have an appreciation of these to allow the PI definition of designing the plant to meet the needs of the process. Mixing-sensitivity characteristics of competitive reaction schemes (Section 2.5.3) can be used to infer chemical reaction rates. Kinetic investigations using a stirred vessel have been suggested by Hearn (1996). In stirred vessels, the local turbulent energy dissipation rate can vary significantly throughout the vessel. If the reaction is slow, the reactants will be fully blended before the reaction occurs, so varying feed pipe position between regions of different turbulent energy dissipation rates will have no effect on product yield. Faster reactions will tend to occur in a small reaction zone near the feed pipe, so product yield would be expected to vary depending upon the local mixing conditions as the feed pipe position is moved. Increasing the number of feed pipes for a given additive amount will also benefit faster reactions by reducing the mesomixing timescales, so the reactions become micromixing limited.

Batch-dump experiments, involving adding all the reactants at once rather than over a period of time, to determine the kinetics of a reaction have been proposed by Etchelles (1997). Adding reactants slowly to a beaker means it is not possible to determine exactly how fast the reaction takes place. By adding all the reactants at once, it should be clearer whether the kinetics are fast or slow. This depends upon having some means of measuring the rate of reaction. Physical observation is possible, for example colour change, or rate of temperature change for exothermic reactions.

Etchelles also identified the challenge of developing a tool for using high intensity continuous experiments in the laboratory, which were based upon using scaled down static mixers. Continuous experiments have been operated in a microchannel reactor by Ramshaw (1999). Operating at 5m/s, a 1m length reactor with an inner diameter of approximately 0.1mm would have a residence time of 0.2 seconds. By using channels of different lengths, the residence time can be changed and reaction kinetics inferred by finding how long the reaction requires to go to completion. The microchannel approach is restricted to low viscosity liquids.

The procedures described above are mainly concepts and not widely used in the laboratory. The area of experimentation is one that will require further examination to develop tools and procedures to aid in the examination of PI potential.

2.8 BARRIERS TO PROCESS INTENSIFICATION

Despite the significant benefits to be achieved by using PI, it has yet to gain wide recognition and application in industry. Part of the cause is the procedures taken during process development, as described above in Section 2.6 and the lack of experimental verification, shown by Section 2.7. There are several other prominent reasons, which are outlined below. Many of these are discussed by Kletz (1998b).

There is a reluctance to use anything other than conventional equipment, as novel equipment may provide unforseen difficulties, which can be termed conservatism. An article by Jones *et al* (1993) on how to reduce development time illustrates this by including the following advice: "Use proven batch processes, rather than committing to develop a new continuous one; avoid new or non-standard equipment wherever possible". This is summed up in a general saying in the chemicals industry of "To minimise risk, minimise innovation" (Industrial Communication, see Appendix A).

Many processes are designed to fit into existing or familiar plant to minimise project

timescales. In larger companies two production plants can be developed in parallel. One of these utilises existing plant for initial production, compromising selectivities and conversion for speed to market. The other plant will be used for long-term production. This parallel development allows more development time for the final plant and therefore allows the consideration of more novel processes (Jones *et al* (1993) and Industrial Communication, see Appendix A). Second generation plant, where a replacement plant for an existing process is desirable, may also benefit from this increased development timescale. However, additional capacity is usually needed as quickly as possible, which is achieved by building a plant the same as the current one (Industrial Communication, see Appendix A).

Innovation is less likely to be applied to bulk chemicals plants as these cost many millions of pounds, so investing in new technology would be a huge gamble. In the fine chemicals industry, it is cheaper to re-use existing equipment which is already fully depreciated, with proven performance and reliability. There are still opportunities for the application of PI in the fine chemicals industry as the financial risk will be lower. A flexible, reusable PI plant can be envisaged where the pipework and civil engineering remain the same, with small intensified reactors that can be inserted as required for each process.

PI is particularly suited to fast reactions, but many reaction schemes have complex chemistry and slow intrinsic reaction rates. One example is a fine chemicals process which has 24 addition and operating steps, requiring three weeks to be fully processed, with some individual reaction stages taking 48 hours (Industrial Communication, see Appendix A). STRs allow numerous processes like these to be run, but PI equipment cannot deliver such long residence times and also may not be able to cope with heavily fouling systems.

The awareness of PI has to be raised. During the course of this research, experienced chemical engineers have been found who completely lack any knowledge of PI and the novel technologies being applied. Streiff & Rogers (1994) wrote that relatively few

engineers were aware of the growing use of static mixers as reactors. Universities that teach PI are in a minority, so graduates tend to know about designing standard unit operations, rather than seeking out more innovative solutions.

The lack of clear design procedures for PI limits its application, as industry does not know how to approach the use of PI. Kletz (1998b), states "Designers, especially process engineers, need some sort of procedure or aide-memoire to help them consider the various ways of intensifying". Such procedures would provide a basis for overcoming many of the other PI barriers. Borland (1996) notes the lack of methodologies for examining the prospects for intensive processing stages. Mallinson (1997) identified the need for a system which gives advice in a timely fashion to promote the consideration of PI early on in process design. Therefore there is the need for a structured approach to PI that identifies all the key decisions that have to be made throughout process development.

2.9 SUMMARY

Process intensification arose out of the desire to reduce the capital cost of chemical plants. It has since become recognised as a means of improving plant safety and the efficiency of processes. Whilst there is no single widely-accepted definition of PI, it should not be considered as simply using novel equipment for chemical processes, but instead that it relates to the whole approach of designing the plant to meet the needs of the chemistry, thereby achieving the most efficient process. The greatest benefits are to be achieved in the reaction stages of the process, as any changes made to the reactor will influence the performance of the entire plant.

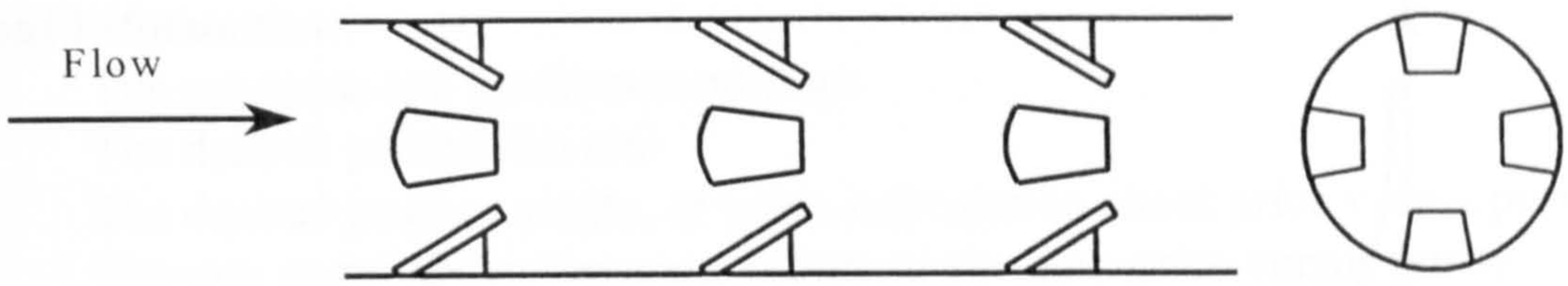
Chemical process development procedures and attitudes have many aspects that require updating if PI is to succeed. The current approach designs a process to operate in standard plant due to confidence in its operation, but this results in inefficient processing due to limited mass and heat transfer capabilities. Other barriers preventing

the wider application of PI include: lack of knowledge of PI technologies and procedures; failure to examine mixing effects on a reaction scheme; conservatism towards novel technology; failure of chemists and engineers to work together.

Examination of mixing effects on a reaction scheme is a key factor in determining the potential for intensifying a chemical process as improving the mixing within a reactor can significantly improve process performance. Competitive reaction schemes, where an undesired reaction occurs over a longer timescale than the desired reaction, will particularly benefit. If the mixing can be completed in a shorter timescale than the timescale the reaction takes, then the desired product reaction will be favoured. Reactor size, residence time and energy consumption are consequently minimised. Improved heat transfer is also required for intensification of exothermic reactions, needing heat transfer equipment that is capable of removing the heat of reaction as it is released. Intensified reactor-heat exchangers have been developed to achieve this.

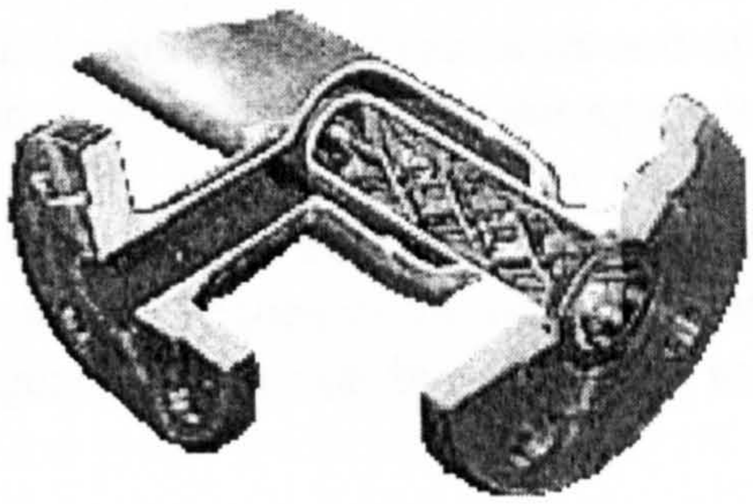
Failure to run small scale experiments under the same conditions as experienced within a large scale plant can cause difficulties on scale-up for both conventional and PI plant. Current experiments do not provide mixing conditions vigorous enough to model PI plant performance. This forms a barrier to PI as its benefits are not identified at the laboratory scale, and therefore the potential for applying PI is overlooked at the very beginning of process development.

All of the above barriers could be removed or made less significant through the application of proper procedures to introduce the concept of PI into process development and demonstrate how to achieve intensified plant design. Methodologies have been published concerning improvements to process development procedures and these are reviewed in the following chapter to examine how the methodologies approach their objectives, and to determine the extent to which PI is referred.



HEV (High Efficiency Vortex)

Kenics



SMXL

Figure 2.1 Examples of static mixer types

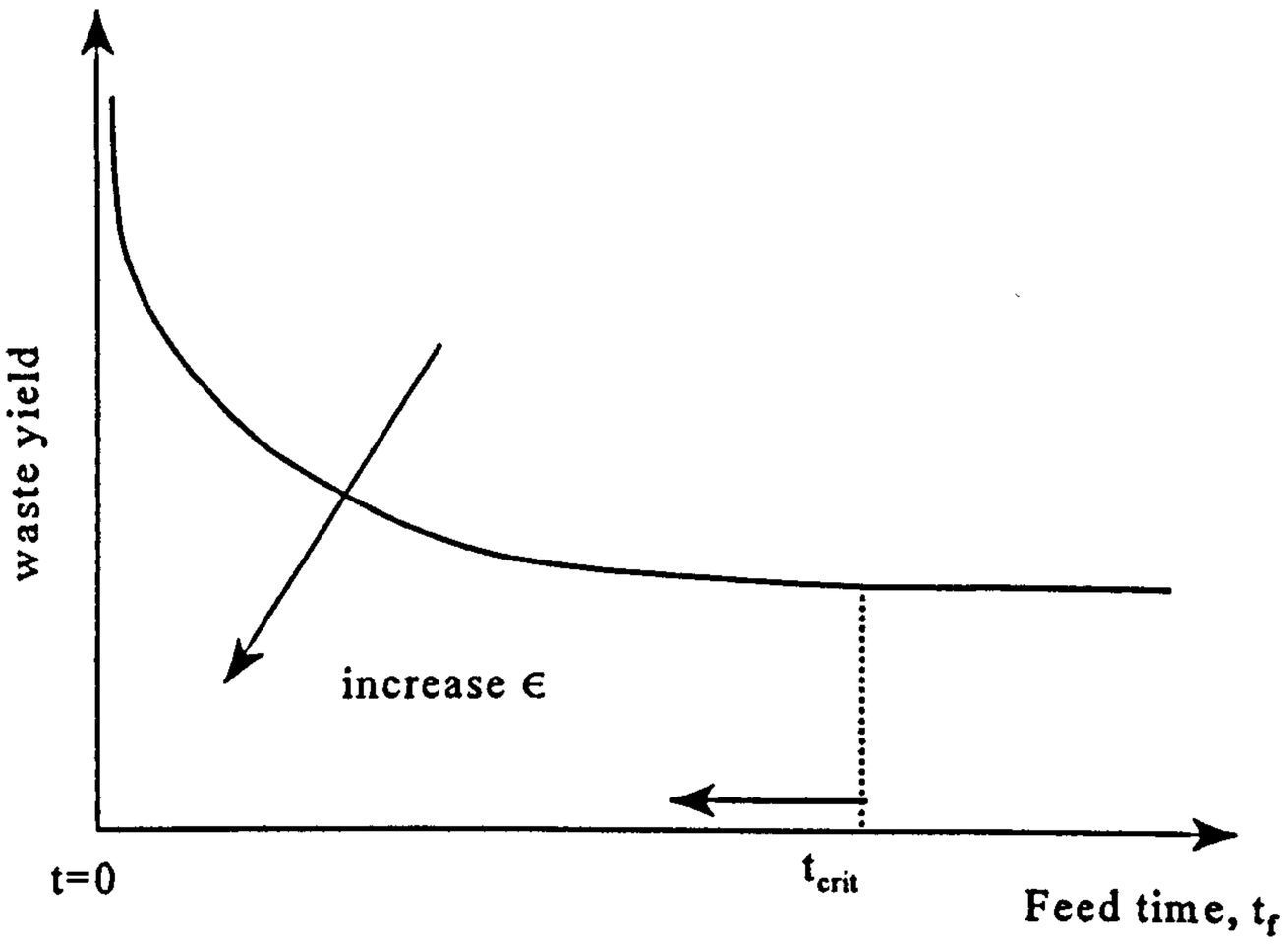


Figure 2.2 Influence of feed time on waste yield in a stirred vessel

Input Information

1. The reactions and reaction conditions
2. The desired production rate
3. The desired product purity, or some information about price versus purity
4. The raw materials and/or some information about price versus purity
5. Information about the rate of the reaction and the rate of catalyst deactivation
6. Any processing constraints
7. Other plant and site data
8. Physical properties of all components
9. Information concerning the safety, toxicity, and environmental impact of the materials involved in the process
10. Cost data for by-products removal, equipment and utilities

Reaction information

1. The stoichiometry of all reactions that take place
2. The range of temperatures and pressures for the reactions
3. The phase(s) of the reaction schemes
4. Some information on the product distribution versus conversion (and possibly reactor temperature, molar ratio of reactants and/or pressure)
5. Some information about conversion versus space velocity or residence time
6. If a catalyst is used, some information about the state of the catalyst (homogenous, slurry, packed bed, powder etc.), some information about the deactivation rate and some idea of the regenerability of the catalyst as well as the method of regeneration (coke, burn, solvent, wash etc.)

Plant and site data

1. Utilities
   - fuel supply
   - levels of steam pressure
   - cooling-water inlet and outlet temperatures
   - refrigeration levels
   - electric power
2. Waste disposal facilities

Figure 2.3 Input information for process design, from Douglas (1988)

CHAPTER 3

METHODOLOGIES LITERATURE REVIEW

3.1 INTRODUCTION

A methodology is a structured procedure for attaining an objective. It can operate as a checklist for items which should be examined, promoting thinking along a desired approach. The lack of structured PI procedures has been identified as a significant barrier preventing the application of PI. A literature review of chemical industry methodologies and the procedures they apply is presented here. A number of the methodologies relate to process development of chemistry and selection of equipment for inherently safe operation. Aspects of the reviewed methodologies where PI considerations could be introduced are highlighted to discuss whether these are capable of being updated for the purposes of being a PI methodology.

3.2 PROBLEM SOLVING ROUTINE

Majaro (1992) has summarised the steps that should be followed when solving a problem into a Problem Solving Routine. This routine can be seen in whole or in part within many of the methodologies reviewed in this chapter.

1. Problem finding - determine exactly the problem to be solved
2. Fact finding - use a checklist to identify and collect all the required data
3. Cause-and-effect analysis - understand the problem's underlying causes
4. Problem statement - state the problem clearly and succinctly, possibly redefining the initial problem so that it is clear exactly what is being looked at
5. Creative idea generation - generate as many ideas as possible
6. Idea screening and feasibility - identify the best ideas and evaluate their feasibility

7. Implementation plan - how to go about putting the ideas into practice
8. Innovation - putting the plan into practice

Steps 1-3 can be achieved through the 'why-why' approach (Figure 3.1). This breaks down the problem into its root causes by systematically asking the question 'Why does this happen?'. The question 'why?' is asked until a final statement is reached that is the most basic possible explanation. The 'why-why' diagram then shows the relationships and relative importance of different parts of a problem.

Problem redefinition, step 4 of the routine, provides a clear set of goals to work towards, increasing the likelihood of a solution. Creative idea generation, step 5, can be achieved through techniques such as brainstorming. Brainstorming involves a team of people, who all understand the problem being addressed and are encouraged to come up with as many concepts as possible to solve a particular problem, regardless of how infeasible they may first appear. Another approach to creative idea generation is the 'how-how' technique, which is a variant of 'why-why'. Each aspect of the problem would be considered and the participants would question 'How can I achieve this?'. A drawback is the problem becoming too fragmented, possibly resulting in an overall solution being missed.

A session held with industrialists on creativity in the chemicals industry, specifically related to innovation and PI (Industrial Communication, see Appendix A), generated similar ideas to those expressed by Majaro. In addition, the team of people required for generation of concepts, was identified. This team should have a diversity of function and background to allow the generation of more concepts, proper discussion and critical evaluation. The following was suggested: Chemists; Chemical Engineers; Safety Evaluators; High Level Management. All must have some knowledge of PI to understand the type of solution desired. Experience of the team should vary. Experience is necessary as the best solution could be related back to previous problems. However, a person with little or no experience in the area may be able to look at the problem without preconceived ideas and generate novel solutions.

3.3 SAFETY AND INHERENT SAFETY METHODOLOGIES

Plant safety has been a significant issue since the incidents at Flixborough in 1974, Seveso in 1976 and Bhopal in 1984, as described by Kletz (1998a). Consequently a number of safety methodologies have been produced. Many of these assess the hazards associated with a chemical process to determine the safest approach to manufacturing a product.

One of the most widely applied safety methodologies is Hazop, the Hazards and Operability study, described in detail by Kletz (1999), that considers the safety of processes once the plant design is nearing completion. The objective is to identify any hazards that may occur and then minimise the chance of these occurring, or reduce the effects of any incident. Hazop uses keywords to rigorously examine every conceivable event on the plant. An example of this is considering a change in the flow rate of coolant to a heat exchanger. Keywords include NO, MORE, LESS and the discussion would cover the possible causes of, consequences of and means of preventing NO flow, MORE flow, LESS flow than that for which the heat exchanger is designed. This approach requires a team of workers to ensure all possibilities are raised and properly considered.

One drawback of Hazop is that plant safety consideration is left until it is too late to do anything other than adding safety systems onto the existing design, making it extrinsically rather than inherently safer. To overcome this deficiency, Kletz suggests that a preliminary Hazop be carried out on the flowsheet before it is passed on for detailed design. This may pick up on significant safety issues and allow major plant modifications to be made.

The Dow explosion index (Dow, 1994), first published in 1964, is stated to be the leading hazard index recognised by industry. It assesses the overall risk from fire and explosion in the event of a major plant incident. The study requires an accurate plan of the plant and process flow sheet. Plant and material hazards, such as inventory,

toxicity, combustibility and operating conditions are graded numerically, with the lowest grading relating to a 'light' hazard and the highest to a 'very high' hazard. Overall hazard rating varies from 'mild' to 'extreme' allowing the different plant options to be compared. The fire and explosion index, like Hazop, is restricted to application when the plant design is nearing completion. As a result, the index cannot be applied to the inherently safe design of chemical plants, though the information acquired may then be applied to a second generation plant by showing where the biggest improvements in safety can be made.

Inherent safety can be applied to both the nature of the chemicals themselves and the plant in which the process is operated. A chemically inherently safe process involves a chemical synthesis route with the least toxic or dangerous compounds. Procedures for the selection of inherently safe chemistry routes have been developed by Edwards and Lawrence (1993) and Cave and Edwards (1997) though these methodologies have yet to achieve application in industry. The approach taken is to rate individual reaction steps in each potential synthesis route for environmental or safety impact. Examples of the features rated are the toxicity of the compounds and the effect on the environment in the event of an incident. A more harmful effect will earn a higher individual rating for each feature. An overall rating is achieved by combining the individual ratings, giving a basis for comparison of the different process routes.

The inventory of materials within the plant is one of the factors required for the comparisons, with high inventories achieving a higher hazards rating. However, Cave and Edwards (1997) say the inventory of materials contained by all the equipment cannot be calculated at the route selection stage where these methodologies are applied, though an estimate for the inventories of the major plant items such as reactors and separation can be made. As there is nothing in these methodologies to determine whether the process can be intensified and operated within small, inherently safer equipment, this inventory is based only upon operation in conventional plant.

An inherent safety methodology was produced by Mansfield (1994). This also uses a

ratings approach where grades on a 1-5 scale are applied to the plant safety measures and the ability of the process to do harm to people, plant and environment. An overall score is derived from the individual scores, with lower scores suggesting inherently safe plant.

A further development of the above inherent safety methodology is the INSIDE - Inherent Safety in Design - project. This provides a comprehensive examination of inherent safety across the whole of process development, including selection of the chemical synthesis route (Schabel, 1997) and design of the plant (Mansfield, 1997). This is achieved through INSET, Inherent Safety Evaluation Toolkits, labelled A to T, which according to Schabel (1997) will "assist the chemists, the engineers, and the designers involved with the plant design process, to identify inherently safer options in an integrated way". These toolkits are intended to make the assessment as rapid as possible, with shortcut tools also provided for occasions when the project timescale cannot support a full evaluation.

The objectives of INSIDE are to encourage the generation of options rather than accepting the first solution through the application of "..guideword based analysis tools that challenge the basis of the initial proposal...to prompt the identification of other ways to achieve the same purpose" (Mansfield, 1996). The guide word approach is similar to the key words used in Hazop where a number of points are set down for consideration at each stage of the design. Ratings are employed throughout the toolkits to allow comparison of the different process options.

Chemical engineers are dependent upon the information given by chemists as the methodology intends them to work separately, even though cooperation between chemists and engineers has been identified by a number of sources as a means of improving process development procedures (Section 2.6.2). Tools are provided for the recording of all steps, but this recording has got to supply the right information to chemical engineers. Tool C, a form for recording information on the chemical synthesis route (Schabel, 1997), includes an area for recording reaction time, but it does not state

whether this is how long the reaction takes in the laboratory, or the inherent kinetic rate. This would prevent the chemical engineers from determining the feasibility for intensifying a process as the true reaction kinetics are not known. Mansfield (1999) confirmed that the time on the form is the time taken to operate the reaction in the laboratory. The tool could easily be modified to clarify this situation

Identification of plant options is first considered relatively early in the INSIDE procedures. These plant options, and hence estimated inventories, are then used in the safety and environmental hazards assessments. As chemists are intended to operate most of this section of the methodology, plant options are more likely to favour conventional technology, even if the challenging tools are applied. There is the danger that the process design may already be frozen by the time chemical engineers get involved, minimising the potential for innovation.

In the plant design stage of INSIDE there are some openings for the consideration of PI. The challenging tool, Tool B, provides prompt words on alternative processing options, for example batch, continuous, STR and in-line, though no specific equipment types are given. In-line mixing is one means of achieving PI, but there are no procedures for determining whether intensification is actually feasible or how selection of the different plant options should be approached.

Despite the interest in the development of INSIDE, it has yet to find a full application in industry. Aspects of the toolkits have been adapted for inclusion in one company's internal procedures and certain parts are utilised on other projects (Mansfield, 1999). The lack of application may be explained from the results of testing with people well-versed in the methodology when Malmém and Suokas (1997) found that the challenging tool to identify process alternatives was not used systematically. A possible reason for this is the amount of documentation required for what is supposed to be a quick and easy assessment tool, which may appear to make INSIDE too complex for many applications.

3.4 EQUIPMENT SELECTION METHODOLOGIES

Methodological approaches have been published concerning selection of the best reactor type and design to run an existing chemical synthesis route. These can be applied to different configurations of an individual reactor type, or selection of one type from a wide range of options.

An approach for deciding when to apply static mixers has been developed by Myers *et al* (1997), consisting of a flowchart, reproduced in Figure 3.2, that shows the main issues and decision points. This could be a useful tool for PI as the static mixer has a high potential to be applied as a PI reactor. However, there are two issues that require consideration. The first of these is the question 'backmixing required?'. If the answer is yes, an STR is recommended. The best approach would be to determine why backmixing is required. If it is to iron out variations in the process feed concentration or flow rate, the upstream processes should be examined to see whether this variation can be eliminated. If backmixing allows a consecutive reaction to take place, a PI loop reactor, as described in Section 4.8.2, could be utilised. Therefore, backmixing should not be used to rule out static mixer operation without further consideration. The question 'plug flow required?' also rules out static mixer operation if the answer is 'no'. It is not clear whether the question is asking whether plug flow is not necessary, or plug flow is not desirable. If it is merely saying that plug flow is not necessary, then this should not rule out the use of a static mixer.

READPERT, the Reactor Development, Selection and Design Expert System (Schembecker *et al*, 1995) interacts with the user to select a full scale reactor type, either backmixed or plug flow, and heat transfer equipment required for a particular reaction mechanism. LARS, Laboratory Reactor Selection (Hanratty *et al*, 1992) was developed to aid the selection of multiphase laboratory reactors. Both READPERT and LARS are Knowledge Based, or Expert, computer software systems where the user supplies relevant information and the system makes quick and consistent decisions. Knowledge based systems (KBS) mirror the decision process taken by an expert to

arrive at an answer to a specific problem. Facts about the process under consideration are inputted and the system then compares these against a knowledge base to infer a solution (McBrien, 1995). The static mixer selection issues developed by Myers *et al* (1997) demonstrate the procedures by which a KBS would consider the available information to generate a decision.

A KBS is used for selecting stirred tank agitators (Lines, 1997). The user specifies the required performance of the agitator which is then evaluated against the agitators in the software databank to select the best one for the particular application. Bakker *et al* (1994) discuss a KBS which allows a user expert to design an agitator in less than ten minutes, as opposed to the two to three hours it would typically take.

KBS approaches have the advantage of being quick and easy to use. A great deal of time and effort is required to build them, but they then permanently capture an expert's knowledge and ensure consistent answers. However, these systems can only recommend what is already known and do not encourage innovation to overcome a particular problem, possibly preventing other, simpler solutions from being suggested.

3.5 BRITEST PROJECT

A major project which started in 1997, a year after the commencement of this work, is Britest - Batch Route Innovative Technology Evaluation and Selection Techniques (Borland 1996). The objectives of Britest are to: halve the total project time from the start of process development to manufacture; reduce the manufacturing time for a product; reduce the capital costs of new investments; produce plant which is inherently more versatile. This will be achieved by supplying chemical engineers and chemists with better tools which can be applied to process development. Members of Britest are listed in Appendix A.

The area of Britest most relevant to PI is the Process Design Group which aims to link

the chemistry to the required plant by matching process requirements to equipment capabilities This will be done through a series of 'envelopes'. Process envelopes define the needs of the plant, such as the operating conditions required, and plant envelopes define the conditions that particular pieces of plant are capable of delivering. The degree of overlap between the plant and process envelopes will then signify the degree of confidence with which the process can be operated in the plant. This is very similar to the PI definition of designing the plant to meet the requirements of the process. Work is also being done on examining means of changing the chemistry and reaction phase to achieve the best operating conditions.

The Britest project is intending to develop similar tools to the PI methodology to examine means of replacing batch processing with more innovative approaches. As a result, this research has been linked with Britest to provide mutual benefits and protect the novelty of this work. This cooperation allowed a wide range of industrial opinions to be incorporated into the survey of PI and process development procedures in the chemicals industry in Chapter 2, providing input to, and validation of, the developed PI methodology.

3.6 RECENT PUBLICATIONS

Approaches to PI have been the subject of recent publications. In particular, Walpot (1999) describes a PI methodology focused on intensification of production processes for fine chemicals. Only the methodological outline is presented by Walpot, with no specific detail on how each of the stages is to be completed. As Walpot's work was published after completion of the PI methodology developed in this work, and two years after it was first published (Appendix D.1), Walpot's methodology has not been included in the main literature survey in this chapter. The similarities between Walpot's methodology and the PI methodology developed through this work, and the implications of this similarity, are discussed in Section 7.10.

3.7 DISCUSSION

This literature survey examined if, and how, PI is currently considered within process development methodologies. References to PI are limited with no specific approaches to the application of PI having been published. A number of related subject areas, including inherent safety which is a major benefit of PI operation, are well represented.

Hazop and the Dow indices have gained wide acceptance and usage within the chemical industry as means of assessing the safety of near-finalised plant designs, but these are applied too late to encourage the design of inherently safer or intensified plants. Other methodologies aim to determine the relative safety of different process options based upon the chemicals present, but do not fully consider the type of plant the process can be run in. Plant design should be considered alongside the chemistry when assessing the overall safety of a process as, for example, it is possible that a process could prove to be inherently safe when running in PI plant, but would be undesirable when running in conventional plant due to the large inventories present.

The INSIDE project encourages the consideration of different plant options, including PI, alongside the chemistry, but does not provide procedures for determining when particular equipment can be applied to a process. If knowledge of PI does not exist, or it is not known that a process can be intensified, then PI concepts will not be generated.

Procedures for determining whether static mixers, a type of PI equipment capable of being used as a reactor, can be applied are available and could be adapted to provide procedures for identifying suitable types of PI equipment for a process. However, these procedures do little to examine the chemistry of the process and determine its potential for intensification.

A ratings system is employed by many methodologies that allows quantitative comparisons to aid identification of the best overall option. Ratings can provide only a general, rather than absolute, comparison of different process routes though this will

allow the best few options to be chosen by showing those which are particularly strong or weak in the most crucial areas of inherent safety. The mathematical approach of ratings can over-complicate the decision procedure, deterring usage (Industrial Communication, see Appendix A).

The inherent safety methodologies have had little uptake, despite being widely presented. One cause of this lack of application is their complexity, arising from the amount of documentation required and the ratings procedures involved.

Lack of consideration of PI is evident in all of the above methodologies, particularly for determining whether a chemical reaction scheme can be intensified. Identification of a suitable PI plant will also require consideration of many factors currently not examined. The INSIDE methodology in particular has the potential for introducing the above PI considerations into the structure and procedures. However, as INSIDE already appears too complex, the addition of the PI aspects would further decrease the likelihood of usage. As a result, a new methodology is preferable that can be developed for ease of application and still allow incorporation of any useful aspects of the above methodologies.

A PI methodology is therefore required that firstly assesses the feasibility for intensifying a process, then gives guidelines on the design of a suitable PI plant. This will serve to fill in the gaps present in previously published process development methodologies and overcome many of the barriers currently preventing the wider application of PI.

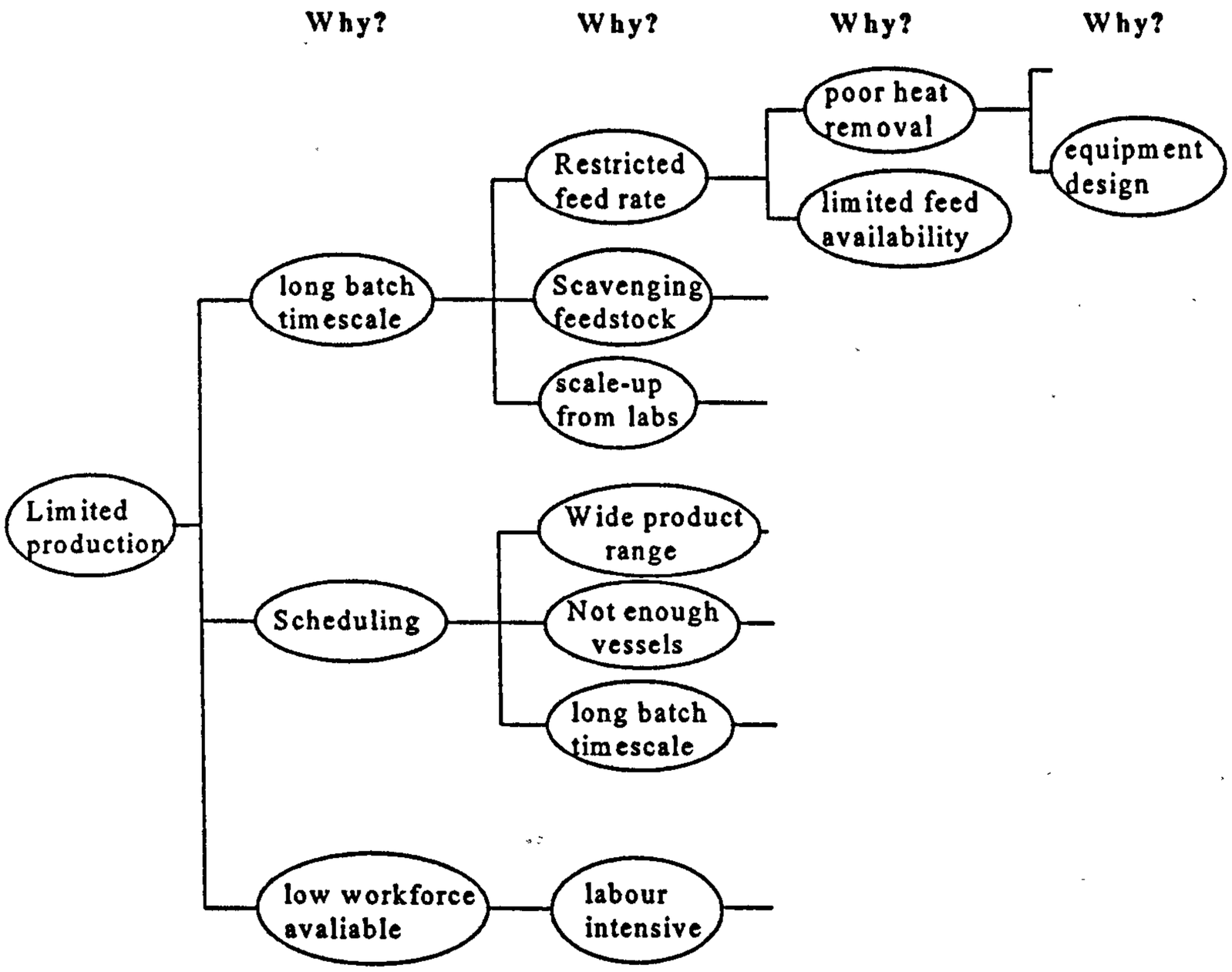


Figure 3.1 'Why-Why' approach to knowledge elicitation

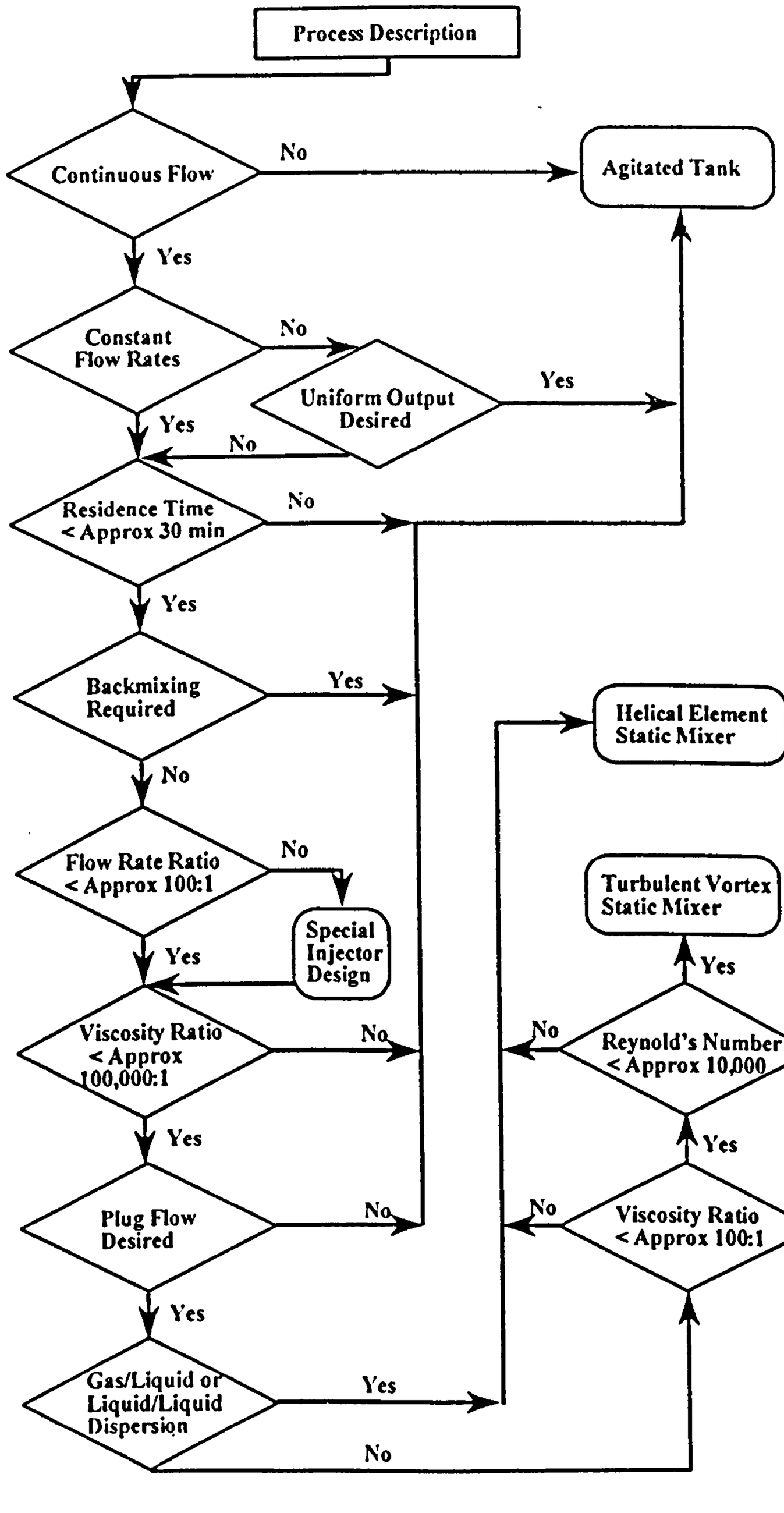


Figure 3.2 Static mixer selection issues from Myers *et al* (1997)

CHAPTER 4

DEVELOPMENT OF A PROCESS INTENSIFICATION METHODOLOGY

4.1 INTRODUCTION

Chemical process development procedures have been shown in Chapter 2 to inhibit the consideration of PI, as too much focus is placed on operation in standard equipment. Therefore, a methodology is required to improve process development practices to allow the consideration of PI. A number of methodologies have been published detailing procedures for improving the safety of processes, reviewed in Chapter 3. Some of these briefly mention PI as a means of achieving safer plants, but there are no procedures on how to approach PI. This shows the need for a new methodology that is specifically related to the application of PI, enabling it to be fully examined during process development. Development of such a PI methodology is described in this chapter.

Development of the PI methodology arose from observing current practices during PI projects and comparing these to the ideal procedures, identifying those aspects that need improving. Four industrial case studies are described that assisted in the development and formation of the methodology, the outline of which became known as the Framework. The case studies tested the format and content of the developing methodology, justifying many aspects of it, but also highlighting areas that should be altered and improved.

4.2 OBJECTIVES

PI can be applied across the entire chemical plant, from reactant make-up through to downstream separation processes. For the purposes of this work the focus will be upon

the reaction stages, as any improvements made here will benefit the entire plant.

It is desirable to select a definition of PI that the methodology should work to achieve. The definition adopted for this research is based upon that of Green (1998) given in Section 2.2, which considers both process and business issues together. As the focus of this work is upon the reaction stage of the chemical process, Green's PI definition is adapted to:

"Process Intensification (PI) is a design approach where the chemical reactor is designed to meet the fundamental needs and business considerations of the process, thereby achieving significant reductions in plant scale and cost, and/or significant improvements in efficiency, process yield, by-product formation and inherent safety."

The two main objectives of the methodology, as identified in Section 3.7, are firstly to examine the feasibility for intensifying a chemical process and secondly to design an appropriate plant. It has been decided to develop a completely new methodology rather than adapting any of the existing approaches, as doing this would simply add to the complexity of these. A new methodology will also allow the ideal approach to PI to be defined without any restrictions imposed by previous work.

From examining process development procedures, two distinct project types can be identified. These are developing completely new processes, and replacing existing plant with a second generation plant. From this, two scenarios have been identified for a PI methodology:

1) New process - identify a new chemical synthesis route, preferably selecting one with the potential for intensification, and then designing a suitable plant
2) Second generation plant - identifying whether an existing synthesis route is intensifiable and then designing a suitable plant

Published methodologies and other literature deal with synthesis route selection

procedures for new processes in some detail. The Britest project (Section 3.5) in particular is producing comprehensive procedures to examine this, whilst the inherent safety methodologies (Section 3.3) are concerned with the selection of chemical synthesis routes. As PI considerations are only one of a wide range of issues that should be considered when selecting a new synthesis route, it has been decided that the PI methodology will be most beneficial when assessing the feasibility for intensification of an existing synthesis route, which applies mainly to Scenario 2 above. Scenario 2 can also allow a more flexible timescale for development of a new plant, allowing more opportunity for novel developments to be considered. As a result, Scenario 2 is used as the basis for the methodology development, with any relevant, or additional, issues relating to Scenario 1 discussed afterwards (Section 4.12).

4.3 FIRST FRAMEWORK VERSION

Development of the PI methodology began by identifying the procedures required to determine the needs of the process and then design the most appropriate plant to meet these needs. Needs of the process are known as 'Process Drivers' and were initially defined for this work as the factors that made the chemical process suitable for intensification. Examples are fast kinetics and liquid phase operation. Taking a process driven approach contrasts with existing equipment driven approach of fitting the chemistry into standard equipment. The basic procedures that should be followed for a process driven approach were identified as:

1) Overview the process to gather information
2) Identify the process drivers
3) Generate possible PI concepts to meet the process drivers
4) Evaluate concepts
5) Select most appropriate solution for full design

These steps are illustrated in a flowsheet, Figure 4.1. The first stage audits the

chemistry of the process, looking at the reactants, operating conditions and kinetics. A checklist approach containing all the required information was identified as an appropriate means of operating the process overview. From this, the process drivers are identified. It was originally envisaged that the methodology would terminate here if it was determined that the process was not intensifiable.

A Concepts Generation stage then takes place where possible PI plant solutions are suggested to meet the process drivers. These solutions are evaluated to determine the best option for full design and construction.

4.4 SECOND FRAMEWORK VERSION

When analysing the procedures in the first framework, a number of other issues that should be addressed were identified. These issues are discussed below, and incorporated in an updated framework, Figure 4.2.

The original process overview covered only the chemistry of the process. Strictly following the PI definition, where a plant is designed to meet the needs of a process, only the chemistry requires consideration. However, a better understanding of the process can be gained from determining how it operates in the existing plant. Any problems experienced during current operation will indicate where attention has to be focused during plant design. If the existing plant is shown to be very inefficient, this will provide an additional justification for building a new plant. The separate stages of the knowledge gathering are termed the Chemistry and Plant Audits.

The chemistry audit is added to by considering whether the reaction scheme could be adjusted to improve the kinetics, as this may make the process feasible for intensification when it otherwise may not have been. Means of achieving this include changing the operating conditions or the use of catalysts. The term 'Laboratory Protocols' is introduced to the audit as a concept for running experiments under the

conditions that can be experienced within intensified plant, thereby demonstrating the benefits of intensified operation.

Plant concepts generation in Version 1 was intended to meet the process drivers, which are based solely upon the chemistry of the process. This results in emphasis being placed on the performance of the plant. However, economic aspects greatly influence the final choice of plant, with the highest performing plant not necessarily being the economically best solution. For example, a long, expensive development time may be required to significantly improve performance, with the overall benefits not paying back this investment. Therefore the economic reasons for improving the process, including improving safety and environmental performance of the plant, should be defined so the plant can be designed to meet both these and the process drivers. These economic requirements have been termed 'Business Drivers' and placed alongside the Process Drivers stage to fully determine the factors the new plant should meet before plant design commences.

Attention should then be focused on those aspects of the process that require improvement. A stage termed 'Rate Limiting Steps' was introduced after the Drivers stage to do this by identifying factors preventing the process running at an increased rate. The rate limiters initially identified were mostly mechanical features such as limited mass and heat transfer in the vessel.

Analysis and selection of the best concept are merged into one stage. A further stage is also added to the methodology to evaluate whether the benefits make it worth building a new plant by comparing the expected performance and costs to that of retaining the existing plant.

4.5 THIRD FRAMEWORK VERSION

Consideration was made on how the methodological approach would be applied to

industrial projects, stimulating further thought on the layout and arrangement of the procedures, resulting in the framework shown in Figure 4.3.

One important new consideration relates to the objectives of the methodology. In the first two versions, the focus was solely on achieving a PI design. However, PI may not be feasible for the process in question, or a PI plant may not be the most appropriate solution. As a result, certain sections of the methodology have been amended to allow the consideration of process options other than full intensification, widening the scope and potential applications of the methodology.

Before the process overview stage, which is renamed 'Knowledge Elicitation', an additional stage is required at the start of the procedures to define the problem that is being examined and the objectives that should be met. This is in line with the Problem Solving Procedure described in Section 3.2. Consequently the Business Drivers stage is introduced as the starting point, as any project to improve a process would mainly be based upon economic and business factors. However, the business drivers themselves are not a problem definition, but a definition of what the solution should achieve. A second Business Drivers stage remains in parallel with the Process Drivers stage to ensure all the objectives for designing a new plant are considered together before plant concepts generation begins.

Process drivers were originally defined for Version 1 as those aspects of the chemistry that make a process suitable for intensification. This definition requires adapting to allow the methodology to be followed even when PI is not feasible. Hence, process drivers are redefined as 'Those characteristics of the chemical reaction scheme that determine the operating conditions in, and required performance of, reactor equipment to allow the process to run at its most efficient rate'. This definition is in line with the PI approach of designing equipment to match the process needs, but applies to all processes whether intensifiable or not.

Chemical rate limiting features are included in addition to the original mechanical rate

limiting features. Examples are slow kinetics or diffusion of reactants into a solid catalyst, where no mechanical improvements can increase the rate of the process. Rate limiting features now allow the feasibility for intensification to be identified, with absence of chemical rate limiting features indicating high PI feasibility. The order of the Rate Limiting Features and Drivers stages is switched to structure the methodology to firstly identify the feasibility of intensifying a process and secondly design a plant.

The concepts generation and selection stages should allow suggestion and consideration of all possible options for improving the process, whether these include full intensification or simple improvements to the existing plant, with the best overall concept being selected.

4.6 CASE STUDY 1

4.6.1 Nitration Process

After the third framework version had been developed, an industrial project was undertaken to assess the feasibility for intensifying a semi-batch nitration process and then design a new, continuous plant (Hearn, 1997). The PI methodology was not in a sufficiently developed format to be followed at the time the project commenced, though the concepts generation procedures were later successfully applied to the project. This case study acts as an observation of the existing, unstructured approach to PI projects, highlighting aspects that proved successful and should be included in the PI methodology, but also showing pitfalls that the methodology should seek to avoid.

The process is a multistage nitration of an aniline compound, operating in a stirred tank reactor (STR). A monohydrate is charged to the vessel, with the aniline compound fed semi-batchwise over a period of five hours to form a hydrosulphate. Oleum is then added over a period of six hours to remove any traces of water. Nitration mixture, consisting of sulphuric and nitric acid prepared upstream, is added over a period of 18

hours, with feed rate regulated to control the bulk temperature of the vessel. The product is drowned out in water, precipitated and filtered to recover the final product.

All reactants in the process are liquid, though solids can exist in the early stages if the temperature drops below a certain value. The last process stage involves crystallisation. By-product formation for the nitration step at full scale operation, which had a batch time of 18 hours, is far higher than that in laboratory production tests, which had a batch time of only 2.5 hours due to the better heat transfer capabilities of the smaller vessel. For the nitration stage, adiabatic temperature rise with stoichiometric addition is 115°C, whilst the maximum desirable rise is 15°C.

4.6.2 Project Procedures

The engineers involved in the project had no prior knowledge of the process. Before the project commenced a PI questionnaire developed by Phillips (1997) was completed by the manufacturer, providing information on materials and process conditions. Another part of the questionnaire requested ratings on the benefits required from the project. These benefits are the equivalent of the business drivers and were particularly useful in determining the manufacturer's needs, showing that the Business Drivers stage is correctly positioned at the start of the methodological framework. The usefulness of the initial information suggests that another stage should be included in the methodology, termed 'basic process knowledge', with a version of the PI questionnaire consequently included in the PI methodology.

The manufacturer was initially interested in intensifying the nitration reaction whilst continuing to operate the rest of the stages in the STR. Knowledge gained during the project showed that all the reaction stages were feasible for intensification and it would be beneficial to have a fully continuous process. This shows that any project scope should be treated as flexible as it may be possible to provide wider benefits than those originally desired.

Information on the process chemistry was requested on the basis of previous experience, with no set list of questions to ask. This stage had to be returned to on a number of occasions to obtain further information. As a result, knowledge gathering was the limiting stage of the project and shows the need for a full checklist of required information to improve procedures. The chemistry audit checklist produced by the time of the project has since considerably expanded and includes many of the points raised during this case study.

The project participants initially examined only the chemistry to assess the feasibility for intensification. However, it was later found to be necessary to examine the current plant to fully understand the process, particularly determining reasons for by-product formation, but also determine if, and how, process performance can be improved. The plant audit strengthened the need for a new plant by showing why the STR is not an efficient way to run the process. This is an issue that had already been addressed and included in Version 3 of the PI methodology. It was acknowledged by the project manager that following even the unfinished PI methodology framework would have prevented this error being made.

The process conditions are extremely corrosive and require a chemically resistant material of construction. At the time of the project it was not clear if intensified equipment would be available in this particular material. If it was not readily available, it would require special, costly, fabrication, or may prevent use of a concept altogether. This shows that more information is required on available intensified plant items to assist in future projects.

Crystallisation in the latter stages of the process could prevent PI application due to the presence of solids. However, it was determined that the correct mixing conditions could control the crystal size, minimising potential for blockages. Solids were already known to be a potential problem in the application of PI, so all of the considerations made during this project were then included in the 'Solids' checklist in the Chemistry Audit, fully described in Section 6.8.1, which aims to promote consideration on means

of overcoming solids formation.

Considering factors that may block the application of PI during the project highlighted that these 'blockers' should be included as part of the methodological approach. As a result, an additional stage taking the form of a checklist of problems to watch out for and potential means of overcoming them is included in the methodology.

Further business drivers were raised as the project progressed. By-product formation was determined to be caused by the very long residence time. Shorter residence times of a PI plant should reduce by-product formation, but this cannot be proven until the process has been modelled under PI conditions. Therefore, there is the potential for removing a downstream purification stage and its associated costs if a purer product can be made. As business drivers can be strengthened or additional ones generated as the project proceeds, this is an additional reason for keeping the Business Drivers stage alongside the Process Drivers stage as well as defining them at the very beginning of the methodology.

One early plant concept was to improve the existing STR by fitting an external heat exchanger loop. This would significantly improve the heat transfer capabilities of the reactor and reduce batch times. However, the complexity of the plant would be increased. Two initial PI concepts were raised as the audits progressed, both based upon technology familiar to the participants. These were a static mixer with cooling jacket and a combined reactor-heat exchanger. It was found that the heat of reaction to be removed would be far too high for a jacketed static mixer to cope with. Also, as the reaction is nearly instantaneous, all of the heat release would occur almost immediately. This means that in any given piece of equipment, only a small fraction of the total heat transfer area would be in contact with the reaction zone and not enough heat could be removed to limit the adiabatic temperature rise. This would rule out operation in a combined reactor/heat exchanger.

Participants in the project restricted all subsequent concepts generation to improving

the initial concepts, rather than trying to identify other operating options. This resulted in a plant concept that, whilst achieving all of the objectives of PI, would be complex to build and operate. A further concepts generation session had to be held to find a more suitable solution. The considerations made during the concepts generation session, including all previously generated concepts, are described below.

4.6.3 Concepts Generation

The process drivers were identified as:

- fast reaction requiring rapid mixing
- very exothermic, requiring rapid heat removal to allow continuous operation
- maximum temperature rise to be limited to 15°C, compared to the adiabatic temperature rise of 115°C

The following heat balance equation can be used to illustrate means of overcoming the adiabatic temperature rise problem.

$$Q = MC_p\Delta T \qquad (4.1)$$

Q is the rate of heat released by the reaction. M is the mass flow rate through a continuous vessel, C_p is the specific heat capacity of the process streams and ΔT the adiabatic temperature rise. C_p is assumed to be constant and ΔT is the variable that requires controlling. This means either 1) Q has to be reduced, or 2) M increased.

1) Reduction in Q

Inhibiting the reaction rate through the use of an appropriate chemical additive would reduce Q and allow continuous operation with heat being released and removed over a period of time. Drawbacks are the extra cost of the additive and additional downstream separation. It would take time to identify a potential inhibitor and examine its effects on downstream processing.

By feeding the additive into the bulk flow in seven separate stages, each followed by interstage cooling, a temperature profile can be produced that does not exceed the desired 15°C temperature rise. Two plant concepts were suggested for operating this way. One was to use a compact reactor-heat exchanger, the Marbond, that is capable of internally adding the reactant to the bulk flow at a number of positions (Phillips, 1999). After reaction in one location, the process fluids pass through a heat exchanger section with all the heat of reaction being removed before the next addition stage is reached. The Marbond was an experimental unit at the time of the project and not available in corrosion resistant materials of construction. As a result, this concept was not accepted as a viable option for the plant.

A second option for sequential addition was a series of seven static mixer reactors, each followed by a heat exchanger unit to remove all of the heat of reaction. This utilises well understood, proven technology with high operability confidence. However, the complexity of the plant would be high, requiring more control and feed addition pumps and consequently is not a desirable solution. Despite the drawbacks, this concept was originally accepted as the proposed design without consideration of any means of overcoming the high number of steps.

2) Increase in M

Increase in M can be achieved by the addition of an inert dilutant to the bulk process stream. This would increase the thermal mass present, reduce the adiabatic temperature rise and allow addition to be done in only one stage. The required flow of dilutant would be approximately six times that of the original stream, significantly increasing the size of the whole plant. However, the high flow rate would increase the turbulence levels, which is desirable for mixing and heat transfer. The cost of adding and removing the dilutant should also be considered.

The product stream could be utilised as the inert mass by employing a recycle around the reactor. This recycle concept utilises familiar technology, but in a novel layout of

which the participants had no previous experience, though a subsequent literature search revealed similar previous applications. This layout only arose as a result of a proper concepts generation session, showing this approach to be necessary. The recycle reactor was accepted as the plant concept as it provided the simplest and most flexible solution to the process and business drivers. Only one unit is required instead of the seven sequential units originally proposed for the plant. It has drawbacks in that product is backmixed with fresh feed, potentially allowing by-product formation. However, long residence time had been identified as the cause of by-product formation, so the vastly shorter residence time of the PI plant should still reduce by-products even with the backmixing.

4.6.4 Additional Considerations

At this stage in the project, the plant manager asked the question "How do I know the PI concept will work?". Laboratory protocol experiments had been considered as a means of recreating intensified operating conditions in the laboratory during the chemistry audit, but this question shows the need for a further laboratory protocol specifically to model a particular concept.

Personnel factors relating to the methodology participants were also noted. Whilst there was no resistance to a PI solution, a quick acceptance of the initial concepts and a subsequent unwillingness to change these occurred. The result was the feasible, but complex, sequential addition reactor. Even when the recycle loop was suggested for the nitration stage, there was still resistance in using this in preference to sequential addition. This highlights the fact that personnel participating in the methodology should be flexible and have an open mind to other options right up until the final decision has to be made.

4.6.5 Conclusions from Case Study 1

Through observing the procedures taken during the project, the following aspects are

added to the methodological approach:

- Basic knowledge gathering section, including project scope, before the audits commence.
- Some means of overcoming solids formation and many other considerations added to the chemistry audit.
- A separate stage for considering PI blockers and means of overcoming them.
- Materials of construction as a PI blocker.
- Means of reducing the emphasis placed on initial concepts to prevent them being accepted before the Concepts Generation stage is reached.
- Laboratory protocol to prove a PI concept.

The following aspects of Version 3 of the methodology framework were justified.

- Business drivers should be considered in the two separate areas.
- A set checklist in the chemistry audit would have reduced the project timescale
- A plant audit was found to be necessary to complete the project.
- The concepts generation session held produced a simpler and more acceptable design than had resulted from an initial concepts approach.

Other aspects highlighted by the case study include:

- Determining the deficiencies of an existing plant through the plant audit can improve PI attractiveness when justifying its application.
- Additional business drivers may arise during the project.
- Personnel should be flexible towards other ideas throughout the methodology.

The case study demonstrates the need for a PI methodology in order to improve current project procedures. The project manager stated that significant time and effort could have been saved had the full PI methodological approach been available and followed at the time.

4.7 FOURTH FRAMEWORK VERSION

The findings from Case Study 1 were incorporated into a fourth version of the methodology framework, shown in Figure 4.4.

A Basic Process Knowledge stage is added alongside the initial Business Drivers stage. As the methodology should be followed by a team of workers from a variety of disciplines, part of the team may have no prior knowledge of the process, which will be provided by this stage before detailed knowledge gathering commences. A PI questionnaire could be used for this purpose. The scope of the project should also be set here, though this may change as the project progresses.

Case Study 1 demonstrates how ideas or concepts occur throughout a project. These concepts will tend to be for applying familiar equipment to the process. The desired methodological approach is to gather all the available information before determining concepts. To account for ideas occurring before the Concepts Generation stage, an 'Initial Concepts' stage was included in the framework so these ideas can be documented for discussion in the proper manner without hindering progress of the rest of the methodology.

The content of both the chemistry and plant audits was expanded considerably. The original chemistry audit asked for the kinetics of the process, but it has become clear through contact with industry that often little is known about the kinetics of processes. Hence some procedures for determining the kinetics are now included in the methodology. Identification of the ideal operating conditions for the reaction has been added, so the plant can be designed to produce these conditions. Mixing-sensitivity experiments of the type suggested by Hearn (1996) and described in Section 2.7 could be applied here.

An addition to the framework is the 'Examine PI Blockers' stage. This considers those features of a process that may prevent PI being applied. The blockers should be

identified and means of overcoming them considered, with as many examples as possible given in the methodology for guidance. Some chemical rate limiting features, such as slow kinetics, could also be included as PI blockers, which is why the blockers and rate limiting features are considered in parallel.

Assessment of PI feasibility is separated from the 'Identify Rate Limiting Steps' stage and forms the mid-point of the methodological approach. This assessment ensures all the required information has been gathered and properly considered. If it is determined that full PI is not possible, continuing with the methodology may still identify improvements to the existing plant that provide significant benefits.

The Process and Business Drivers stage now forms the problem definition for the plant design aspect of the PI methodology. Drivers show what the plant should achieve, both technically and economically, setting objectives for the concepts generation to meet.

A separate Laboratory Protocol stage is added to the PI methodology as a means of simulating PI equipment and proving a chosen concept, providing a design basis for the plant.

Two industrial case studies are now presented, both of which used Version 4 of the methodology framework as a template of procedures.

4.8 CASE STUDY 2

4.8.1 Polymerisation Plant

A project was undertaken to examine the feasibility of intensifying a polymerisation plant (Cropper *et al*, 1999). All project participants were familiar with the PI methodology and its objectives.

Monomer emulsion and additive solutions are made up in stirred tanks located above the main process vessel, which itself is a stirred tank reactor. Feed is charged to the main vessel and mixed at a regulated temperature whilst polymerization takes place. Further solutions are added at the end of the reaction to finish the product, before filtration to remove any solids produced. The major business driver for intensification is the manufacturer's desire to improve their competitive edge through more efficient production of the polymer. It had already been identified that poor heat transfer from the existing vessel was limiting the current production rate. The manufacturer was keen to examine the potential for continuous operation and the project was done with the objective of building a pilot plant.

A set list of required information taken from the chemistry and plant audit checklists, shown in Figure 4.5, was sent to the manufacturers. Supplying the check-list enabled the manufacturer to gather all the available information on the plant and operating procedures. This saved a great deal of time and allowed the detailed information gathering to commence almost immediately.

Very little information was available on the reaction kinetics, so a literature search and kinetic modelling was required to determine these. Kinetic model predictions were made on the rate of conversion of monomer to polymer at different temperatures and these were compared to experiments specifically run at those temperatures. The kinetic model was then adjusted until it matched the experimental results more closely. It was found that at a temperature of 95°C a residence time of three minutes is required for the reaction to go to completion. The current process has a batch cycle time of 28 hours, of which 15 hours is spent processing and the rest on material charging, heating and cleaning duties.

There were gaps in the supplied information relating to heat transfer capability. Although the heat transfer surface area of the existing vessel could be determined, there was limited data on the coolant fluid flow rate, inlet and outlet temperatures. It was necessary to obtain a heat transfer coefficient to use as a basis for the new plant, so this

had to be estimated from the available knowledge. The current vessel is subject to heavy fouling which decreases the heat transfer coefficient over time. A new plant should minimise fouling and provide more efficient heat transfer, so the heat transfer capability may be greater than that estimated for the current plant. As a result, the pilot plant should have flexible heat transfer capabilities to allow for this heat transfer coefficient estimation. This also demonstrates the need for the plant audit as the heat transfer information provided was essential to the design of a new plant.

The request for information on the mechanical stability of the polymer in Figure 4.5 was added by the project manager. It is known that some products may break down when subjected to very high mixing energies and a product that breaks down easily may prevent the application of PI. Mechanical stability was tested by subjecting the polymer to controlled high mixing energies in the laboratory protocol vessel developed for this research and described in Section 5.5. The product was then examined to determine whether the quality suffered in any way due to polymer breakdown. It was found that there was no product breakdown at any turbulent energy dissipation rate up to the maximum available 150 W/kg, which is higher than would be expected to occur in a continuous polymerisation plant.

The only potential PI blocker is the severe fouling nature of the process fluid which could foul the narrow passageways in PI equipment over time. This requires a high shear-rate within the intensified equipment to ensure that fouling is minimised. The equipment should be easily dismantled for cleaning if fouling does occur.

4.8.2 Concepts Generation

The process drivers were identified as:

- Residence time in excess of three minutes to allow reaction to go to completion
- Completely mix the reactants in significantly less than the three minute reaction time to ensure mixing is not the rate limiting step
- All heat of reaction is removed as it is generated

- Fouling is minimised or prevented

The range of equipment that could be suggested was limited by the manufacturer who had a preference for a tubular type reactor.

To prevent the process fluids fouling the pipeline, the fluid velocity has to be sufficiently fast to produce turbulent flow, with a velocity of 3m/s selected. A straight tubular reactor operating at 3m/s and three minute residence time would require an undesirable length of 540m. As a result a loop reactor was suggested, with the process fluids recirculated a number of times to provide the desired residence time in a much shorter length of pipe. The loop reactor also allows flexibility for examining the effects of velocity upon fouling, heat transfer surface coefficient and residence time.

Static mixer inserts are placed at strategic positions within the tubes to promote mixing and plug flow operation. It was considered unnecessary and undesirable to fill the entire length of tubing with static mixers, as very rapid blending is not required and the increased pressure drop would be unacceptable. The static mixer chosen has an open format and is removable to allow easy cleaning should fouling occur.

Two options were considered to provide the heat transfer duty. One is to submerge the entire loop in a cooling bath and the other is to place cooling jackets along the tubes. The cooling bath would be the cheaper option, but the jackets were chosen as these would provide a more efficient and controllable means of heat transfer for pilot study purposes.

4.8.3 Conclusions from Case Study 2

Through observing the procedures taken during the project, the following aspects were added to the methodological approach:

- Literature searches and kinetic models can be used to focus experiments to infer

the reaction kinetics and timescales.

- Testing for mechanical stability of the process fluid is added to the chemistry audit.
- A pilot plant was preferred rather than laboratory protocol experiments. Therefore, a pilot plant option should be placed in the methodology framework to cover this option.

The following aspects of Version 4 of the methodology framework were justified.

- The need for indications on how to infer chemistry kinetics.
- The chemistry and plant audit checklist to aid gathering of information.
- The plant audit to supply information required for designing the new plant.

Other aspects highlighted by the case study are:

- The concepts generation section may have constraints placed upon it by the desire for a certain type of plant.
- Further operational concepts can be generated around a particular type of equipment, for example with heat transfer provision for the loop reactor.

The success of the plant design cannot be fully evaluated until the pilot plant is constructed and commissioned. The timescale of construction does not allow for any evaluation to be included in the thesis.

4.9 CASE STUDY 3

4.9.1 Independent Case Study

This is a project undertaken by two chemists and two chemical engineers, two of whom had prior knowledge and experience of the methodology but were not involved in its

development (Cheung *et al*, 1999). This case study therefore serves as an independent test of the PI methodology procedures. Version 4 of the methodology framework was referred to throughout to ensure all of the major steps were considered, though the full detail of the methodology was not used by the team.

The process is a polymerization reaction. A liquid reactant and a solvent are charged to the stirred vessel with a monomer in the form of small flakes of solid which melt in the bulk liquid. By-product formation currently limits the product yield to 95%. Viscosity increases substantially over the course of the polymerization. The project business drivers are to increase conversion from 95% to 99.5% whilst producing a more consistent product quality.

The chemistry audit was run with the team specifically looking for any chemical rate limiting features, blockers or PI opportunities. Limited information was available on the kinetics, though a different type of catalyst was suggested to significantly increase the reaction rate. Temperature and solvent type were experimentally examined as a means of increasing reaction rate, with the solvent known to catalyse the reaction to a certain extent. Under ideal operating conditions, required residence time is approximately 100 seconds.

By-product formation was determined to occur at approximately 1/10th the rate of the main reaction. The plant audit suggested that the by-product formation results from localised high concentrations of additive, which is added as solid flakes and dissolves only slowly in the vessel where the temperature is only slightly higher than the solid melting temperature.

It is possible that the thermodynamic equilibrium of the reaction could prevent any more than 95% conversion. This would then remove one of the major drivers for intensification unless the product can be separated as soon as it is formed, shifting the equilibrium in the favour of higher conversion. However, it was later shown that 100% conversion is possible in this case.

4.9.2 Concepts Generation

Plant concepts were generated to meet the process drivers of:

- reducing the high localised concentrations of solid feed
- residence time of approximately 100 seconds
- ensure increasing viscosity of the polymer stream can be handled

Concepts to aid dissolution of solid feed into the bulk liquid include: using powder instead of flakes; multiple feed points into a vessel; rapid mixing; pre-melting or dissolving of the solid before addition; higher temperatures of operation.

The equipment concept suggested to meet the drivers was a static mixer/heat exchanger arrangement which can handle the size of solids used in this process. The high operating confidence in this type of equipment played a large part in its selection. A novel step was required to cope with the increasing viscosity as polymerisation progressed. Static mixers are available in different types for particular blending duties, so a single mixer type would not be optimal for the entire process. To meet the requirements, different types of static mixers are placed in sequence to provide the best possible mixing with the viscosity at that location.

4.9.3 Conclusions from Case Study 3

Additions to the methodological approach arising from Case Study 3 are:

- Consideration of chemical equilibrium added to both the chemistry audit and the PI blockers checklists.
- PI blockers were focused upon throughout the project, indicating the areas of the process that should be preferentially examined to overcome these blockers. This shows that the blockers should be consulted and considered throughout the audit sections, rather than only after the audits.

The following aspects of Version 4 of the methodology framework were justified:

- Layout of the methodology framework ensured all the important factors were considered in the preferred order.
- The plant audit proved beneficial in revealing the causes of by-product formation.

4.10 FIFTH FRAMEWORK VERSION

Case Study 3 demonstrated that there is an interaction between the chemistry audit and the PI feasibility assessment, particularly through the PI blockers. Potential PI blockers should therefore be kept in mind throughout the methodology and means for overcoming them considered as they arise. The framework, Figure 4.6, is updated by indicating the interaction between the audits and the blockers with a double-headed arrow. It is also recommended in the PI methodology introduction that participants familiarise themselves with the PI blockers section before commencing the audits. A PI blockers summing-up stage is still required to allow the feasibility to be properly determined and concluded.

The case studies have proved to be particularly valuable in assessing the developing methodology and adding content to make it more widely applicable. It is possible that additional items can be added to the methodology, updating or changing the content of the separate sections. As a result, all projects should be written up as PI case studies after completion, highlighting important points and lessons learned which may improve procedures in future projects, though this is not included as a formal methodological stage.

Version 5 is the final format of the PI methodology framework and is fully described in Chapter 6.

4.11 CASE STUDY 4

4.11.1 Concepts Generation Study

During a PI workshop attended by a number of industrialists and academics, listed in Appendix A, a session was undertaken to generate concepts for a process. This provides a case study on how the Generate Concepts stage operates in practice. All the information on the process was gathered through the Britest project (see Section 3.5) and then presented in a manner following the PI methodology up until the concepts generation stage.

The process consists of two aldehydes, E and F, reacting in the presence of a catalyst to form an aldol, G, with reaction rate constant k_1, and by-product formation of a diol, H, with reaction rate constant k_2. The outline reaction scheme is:

$$\underset{\text{desired reaction}}{E + F \xrightarrow{k_1} G} \qquad \underset{\text{byproduct reaction}}{E + G \xrightarrow{k_2} H} \qquad \text{Liquid phase catalyst} \qquad (4.2)$$

Water and catalyst are charged to the stirred tank reactor (STR) and aldehyde F added semi-batchwise. The vessel contents are heated up with the second aldehyde being added after this time. Rate of addition is restricted due to limited ability for removing heat of reaction. Finally the temperature is raised and maintained to increase yield, with the reaction stopped when diol concentration reaches 5%.

At the current temperatures of operation (70-95°C) the reaction kinetics are such that the reaction could go to completion within one hour if free of mechanical rate limiting features. All process materials are liquid at these temperatures. The difference between the reaction rate constants, k_1 and k_2, increases with temperature, favouring the desired reaction. The potential for operating at a higher temperature was discussed as an operating concept, either under pressure for liquid operation or as a gas-phase reaction. This has not been experimentally tested.

4.11.2 Concepts Generation

An open session was held to generate concepts for the plant. Participants were from a wide variety of backgrounds, including chemists and engineers, and experience varied from those new to the concept of PI through to experts in the field. The options generated, and issues relating to them, are discussed below.

1) Pressurised shell and tube reactor

Working on the basis of a combined reactor-heat exchanger, this arrangement will allow rapid preheating of the reactants to the reaction temperature, and removal of heat as it is generated to maintain that temperature.

2) Tubular reactor

One long tube with heat transfer taking place out of the vessel walls. Potential length of the reactor may be a drawback.

3) Static mixer

Tubular reactor with static mixer inserts to provide plug flow operation.

4) Compact reactor-heat exchanger

A particular compact reactor-heat exchanger that can operate at very high temperatures and pressures of up to 300 bar is available. This may allow the reaction to go to completion in seconds.

5) Loop reactor

A tubular reactor with a recycle loop to provide higher mean residence times than those that may otherwise result in an unfeasibly long tubular reactor.

6) Fit a heat exchanger loop to the existing STR

Operates at the current temperature and pressure in the existing vessel, but should improve heat exchange performance enough to significantly reduce the batch time.

7) Reflux on existing STR

Allows a higher temperature of operation, with any liquids that boil off being condensed and returned to the system. The boiling action would act to remove heat of reaction, with the heat exchanger on the reflux being more efficient than the current cooling jacket heat exchange equipment.

During the session, all of the first concepts (1-5 above) consisted of options to replace the existing reactor with smaller, more novel equipment, particularly operating at increased temperatures and pressures. Whilst this is the overall objective of PI, all potential plant options should be considered, as those relating to improving the existing plant may be the most cost-effective option for improving performance. After this was brought to the attention of the participants, the final two options for improving the existing STR were raised. It was suggested by a participant that this occurred as the emphasis of the whole presentation was on PI, which set the team thinking along this approach. Had the case study been introduced to a team outside of the PI workshop, most of the options would likely to be based only upon improving the STR. This highlights the plant-constrained approach which can be a barrier to PI due to the failure to consider other operating options. However, in this case the plant constraints operated the other way around where only PI was considered at the expense of more conventional solutions. This shows the need for the methodology participants to be completely open-minded to the process solution.

4.11.3 Conclusions from Case Study 4

The concepts suggested involve both the equipment and the operational procedures. By increasing the temperature and pressure, the rate of reaction could be significantly increased, reducing required residence time and therefore allowing the use of smaller equipment. Combined reactor-heat exchangers and tubular reactors form the basis of the PI plant options. Despite the limitations of the exercise, mainly the lack of time to do a full concepts generation and assessment session, it is shown that the

methodological approach presented the information in a manner that allowed rapid generation of solutions to meet the identified drivers.

4.12 APPLICATION OF THE PROCESS INTENSIFICATION METHODOLOGY TO NEW PROCESS DEVELOPMENT

The PI methodology framework focuses on situations when existing plant is to be upgraded or replaced. However, great benefits can be achieved by considering PI during the development of completely new processes. This section discusses how the PI methodology could be applied in the earlier stages of process development.

Current process development procedures are described in Section 2.6. From the identification of a target product, these can be summarised as:

1) identification of a large number of possible synthesis routes
2) initial screening to remove obviously infeasible routes
3) more detailed screening of remaining routes on the basis of cost etc.
4) final synthesis route choice
5) plant design

Figure 4.7 shows where PI considerations would fit in with the existing procedures. It is common for chemists to control most of the process development, with chemical engineers only becoming involved in the later stages when it may be too late to consider other synthesis routes or operating options. To allow the consideration of PI, chemists and chemical engineers should work together throughout the procedures. Prior knowledge of the PI approach and philosophy is a requirement, though detailed knowledge is not essential.

The first occasion PI should be considered is during the initial synthesis route screening. This is when process routes that are obviously infeasible are discarded from

further analysis. The role of the PI consideration will be to ensure that fast reactions which may be suitable for intensification are not screened out on the basis of being difficult to handle or control in conventional equipment. When the choice of synthesis routes is subsequently narrowed down, the remaining ones are evaluated on cost, environmental and safety issues. An idea of the form and size of plant is required for this evaluation. As PI plants can be significantly smaller, safer and cheaper than conventional plant, it will be necessary to have quick procedures for examining the synthesis route for PI feasibility before evaluating what the plant may look like.

Experiments that are currently carried out on potential synthesis routes could be expanded to examine the potential for intensifying the route by examining any effects of mixing. Some aspect of the chemistry may give an immediate indication of the potential for intensification, such as the general reaction type if it has previously been identified as intensifiable. To obtain required information, sections of the methodology chemistry audit can be utilised, with the minimum information required being process phases, physical properties and an appreciation of the kinetics.

The feasibility of intensifying the process can be assessed by the procedures outlined in the PI methodology framework by determining any potential PI blockers. This will allow identification of a general plant type, or types, in which the process could operate. A database of potential plant options and operating capabilities would be useful for this stage. The inventory and costs of these options can then be estimated and compared. This estimation and subsequent comparison to other routes could be carried out in a manner similar to the inherent safety methodologies described in Section 3.3, which rate individual considerations before combining them into an overall assessment. Once a particular synthesis route is selected, the full chemistry audit should then be applied and the PI methodology framework followed from there on.

4.13 SUMMARY

Development of the PI methodology was based upon the procedures required for designing the plant to meet the needs of the process, meeting the definition of PI. The resulting methodology is a paper-based flowsheet, known as the Framework, which developed in both format and content over the duration of this research. Case studies have served to test the methodology, justifying the format and content whilst suggesting some amendments that were required to increase its applicability. A full description of the Framework and the content of each of the methodological stages is given in Chapter 6, and it is discussed in Chapter 7.

The methodology requires experiments to model the performance of intensified equipment in the laboratory. This will serve the purposes of demonstrating the benefits that can be achieved through intensified operation, and simulating a particular plant concept. This may prove crucial in improving confidence in PI operation and therefore increase the likelihood of it being applied. These experiments have been termed a 'Laboratory Protocol' and are developed further in the following chapter.

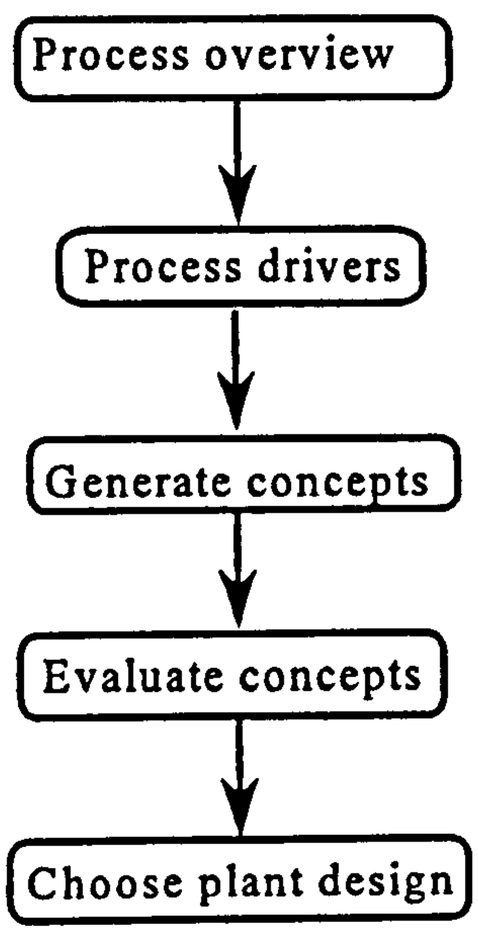


Figure 4.1 First version of the PI Methodology Framework

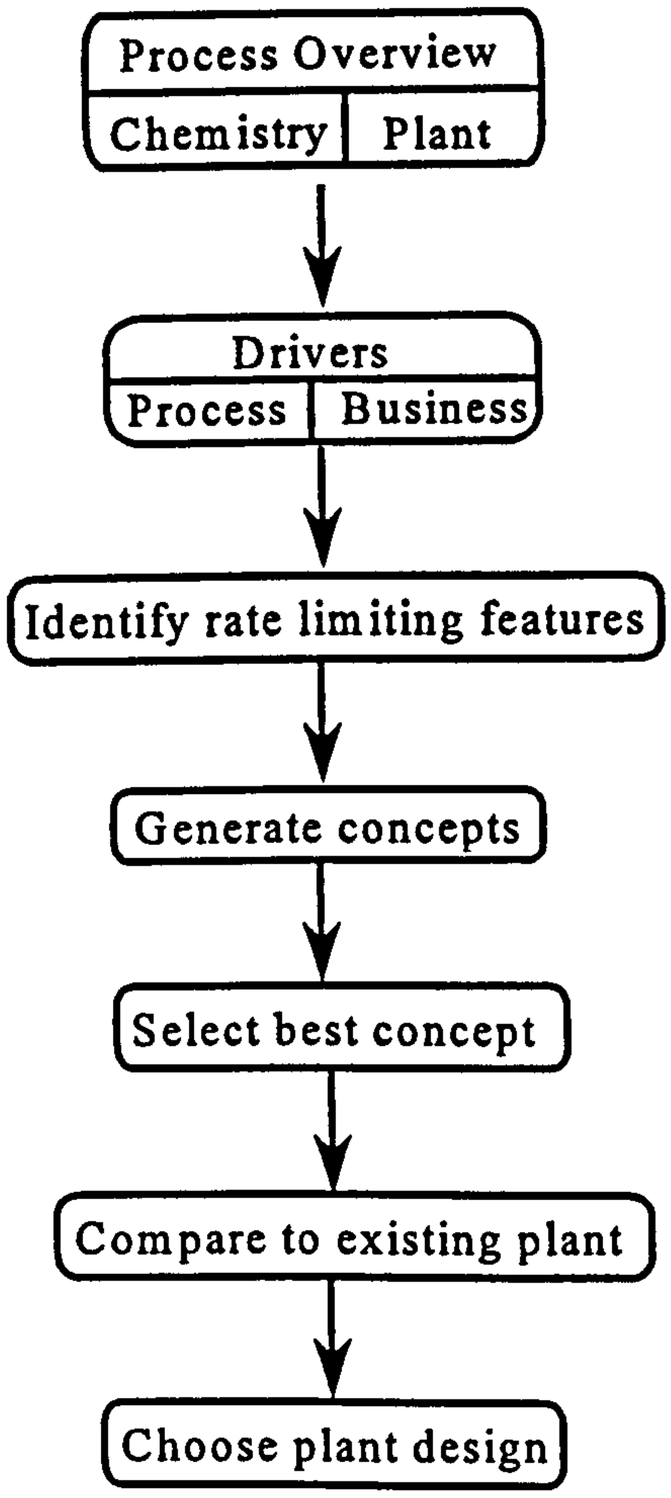


Figure 4.2 Second version of the PI Methodology Framework

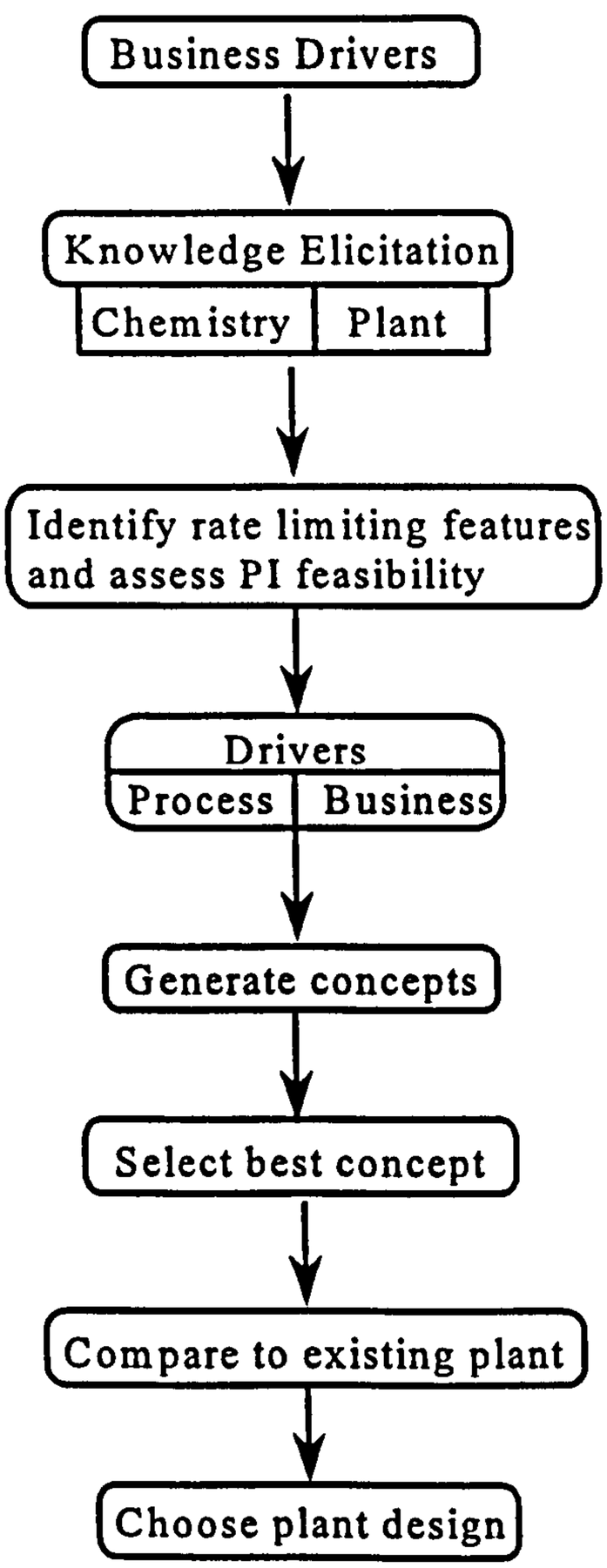


Figure 4.3 Third verison of the PI Methodology Framework

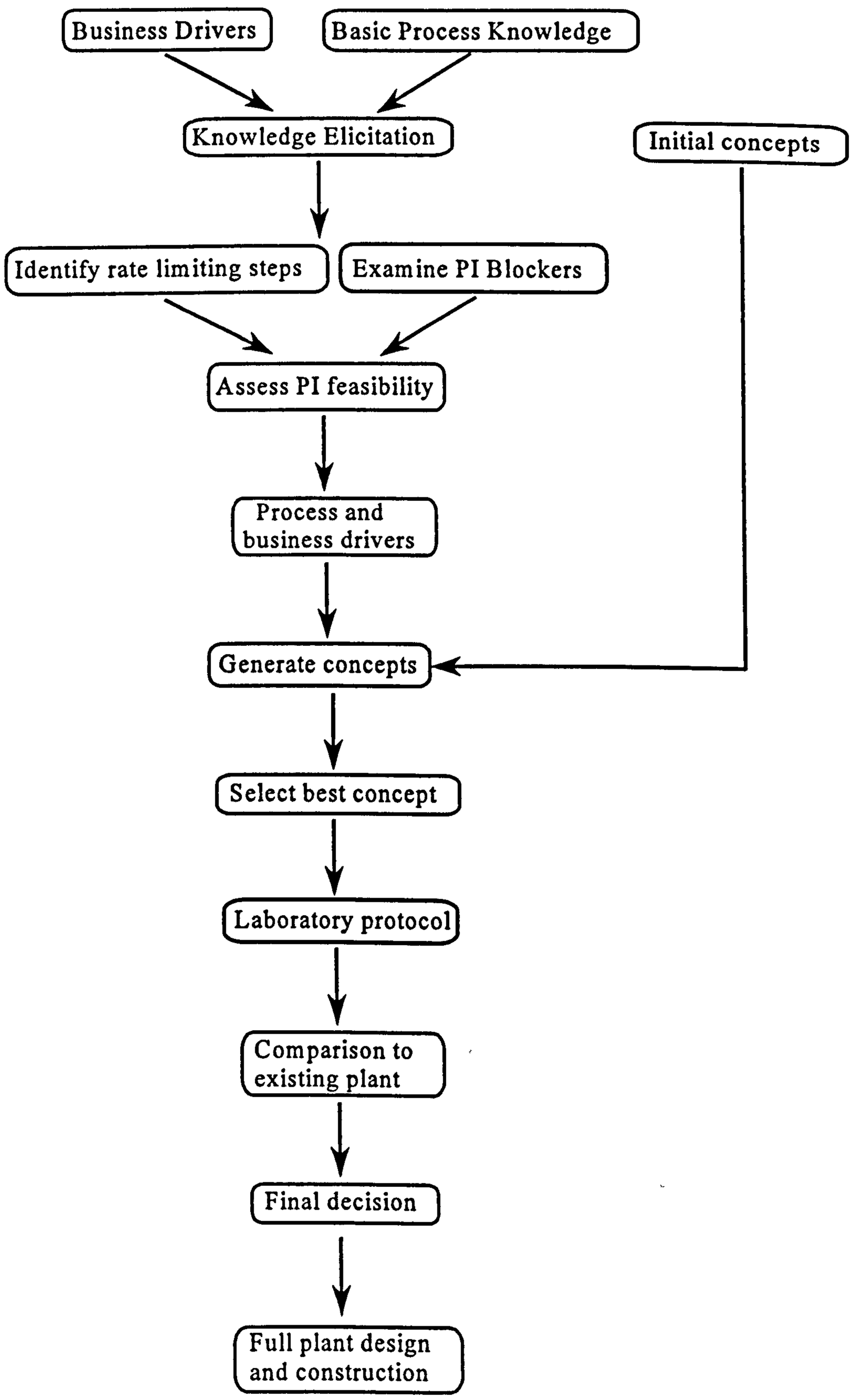


Figure 4.4 Fourth Version of the PI Methodology Framework

Chemistry Audit

- reaction scheme
- order of addition of reactants
- magnitude of heat release
- rate of heat release
- kinetics of reactions
- physical properties of process fluids
- corrosiveness
- ideal operating conditions
- minimum/maximum operating temperatures
- mechanics of byproduct formation
- solids formation
- residence time required
- mixing sensitivity of the reaction scheme
- mechanical stability / maximum mixing intensity

Plant Audit

- physical dimensions of reactor and other equipment used
- materials of construction and limitations
- operating conditions
- mixing capability
- heat removal capacity
- how and where feeds are added
- rate of feed addition and why
- length of batch times
- order of feed addition
- current production output
- current production rate
- utilities available
- upstream and downstream processing capacity and storage
- obvious rate limiting features
- flexibility of plant for making other products
- mass balance
- heat balance

Figure 4.5 Audit questions for Case Study 2

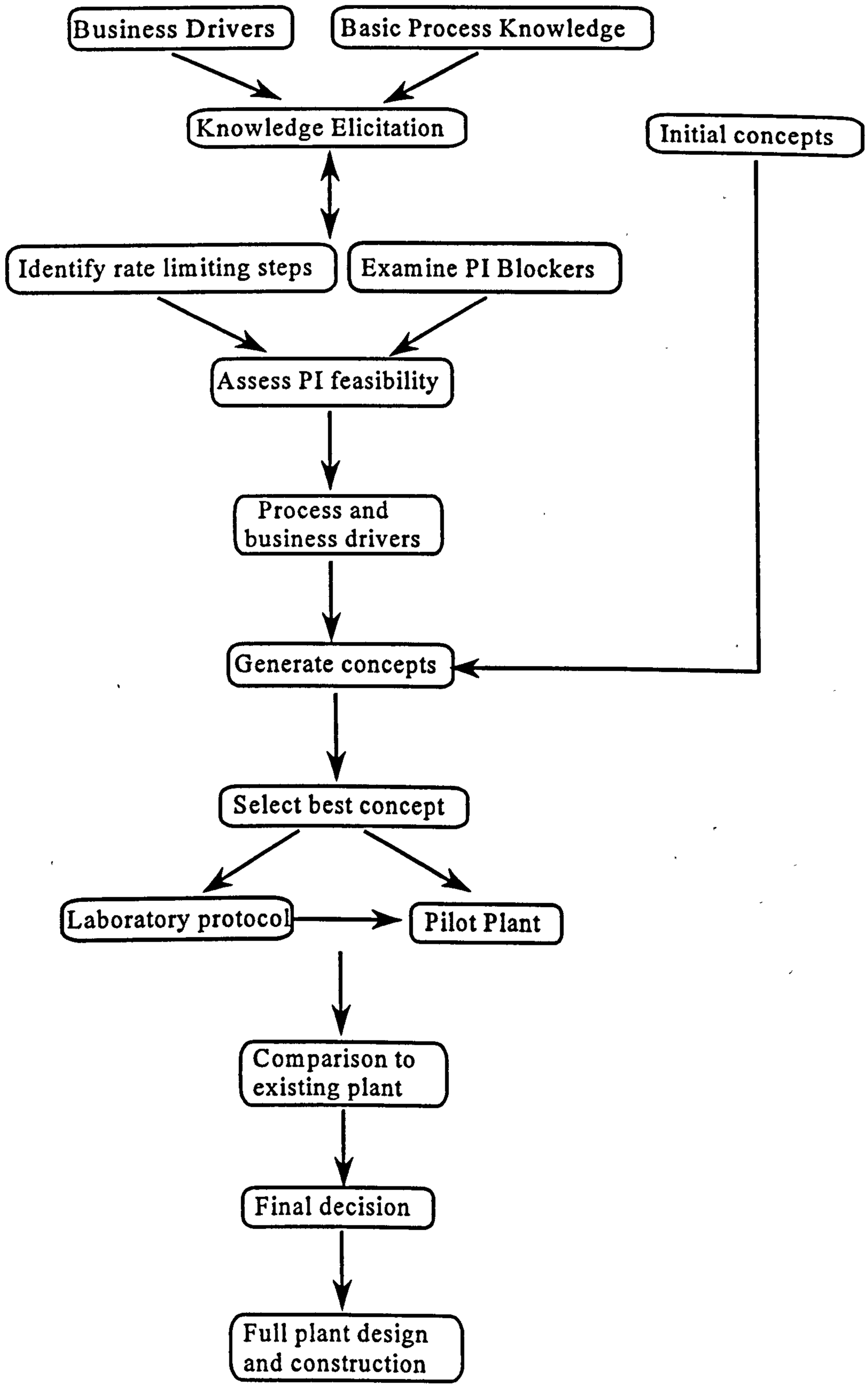


Figure 4.6 Fifth version of the PI Methodology Framework

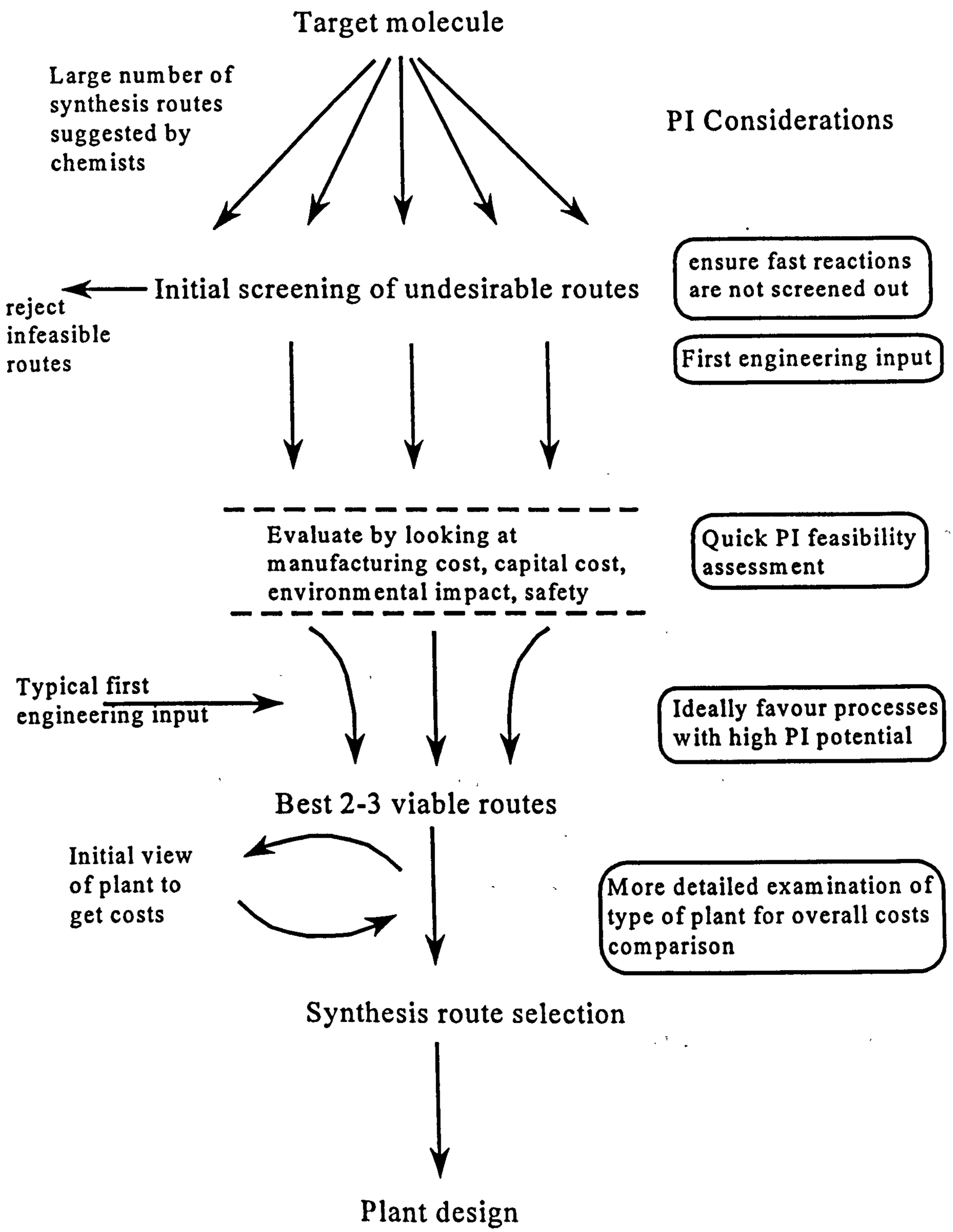


Figure 4.7 Where PI should be considered within existing synthesis route selection procedures

CHAPTER 5

LABORATORY PROTOCOL

5.1 INTRODUCTION

There are many factors that restrict the consideration and application of PI during process development. One of these factors is the inability of small scale experiments to recreate the conditions experienced in a PI plant. As a result PI cannot currently be modelled within the laboratory, which limits confidence in operation and can prevent application. To overcome this problem, the PI methodology incorporates the concept known as a laboratory protocol. This is a set of experiments that are run under the same reaction environment as would be experienced in a full scale plant.

An investigation has been made into the equipment and procedures required for the laboratory protocol. This chapter describes how the approach was developed, leading to a design for the protocol equipment which utilises the novel concept of simulating continuous, intensified operation in a semi-batch stirred vessel. Experimental testing has been undertaken which shows that the protocol approach works in practice, though future work is required to develop the concept and tools further.

5.2 MODELLING PROCESS INTENSIFICATION IN THE LABORATORY

Procedures that should be followed for PI to be successfully modelled in the laboratory can be summarised as follows, as shown in Figure 5.1:

1) Experimentally determine the best operating conditions
2) Select the plant equipment that can most closely provide these conditions
3) Calculate from correlations the expected mixing conditions that the equipment will actually provide

4) Run protocol experiments under the same conditions that would be experienced within the plant to simulate and prove the concept

5) Repeat above steps (2-4) if required performance is not achieved. Otherwise, design full scale plant.

Plant concepts are generated and selected on the basis of being able to provide the best operating conditions required by the process. However, it may not be possible to match all of the required conditions, with some compromises having to be made. This is the reason that an additional laboratory protocol is required to model a plant concept to prove its operation. It is the modelling of plant concepts that forms much of the work in this chapter.

One difficulty in the above approach is knowing in advance the conditions that would be achieved within the full scale PI plant. The Britest plant performance envelopes (Borland, 1996), aim to characterise many different types of equipment showing the range of conditions each is capable of providing and would hence be of great assistance at this stage of the methodology.

For the purposes of this work, static mixers have been chosen as the PI equipment to simulate. A wide range of design information and mixing performance prediction is available on static mixers, discussed in Sections 2.5 and 3.4. Static mixers have found many applications for blending and reacting liquids as they are a simple and cheap option for intensifying a plant. Two approaches may be required: The first is to model the performance of a particular static mixer design; the second is to choose the best possible static mixer design.

To follow the procedures in Figure 5.1 assuming a static mixer has been selected as the plant option, the operating conditions within the static mixer have to be identified. Information required includes: the static mixer type and geometry; bulk flow rate through the mixer; additive flow rate and its ratio to the bulk flow rate. From this mixer information, turbulent energy dissipation rate and characteristic mixing timescales can

be determined. Protocol experiments should then be run to achieve the same turbulent energy dissipation rate and characteristic mixing mechanism timescales. Procedures for calculating these are described in Section 2.5.2.

The rest of this chapter describes how the protocol vessel and experimental technique was developed to test the above procedures. A previous study into the performance of an SMXL-type static mixer (Wadley, 1996), is used to provide a direct comparison between the protocol and static mixer operation.

5.3 OPTIONS FOR THE LABORATORY PROTOCOL APPROACH

A design for the laboratory protocol equipment had to be identified. Potential approaches for simulating PI operation have been reviewed in Section 2.7 and these are now examined to find the most applicable method. The equipment selected should produce a wide range of mixing conditions to allow its application to as many situations as possible.

To simulate continuous, intensified static mixer operation at the laboratory scale, the natural approach would be building a small scale continuously operating rig incorporating static mixers, as suggested by Etchelles (1997). The range of conditions that can be provided by a particular static mixer is limited, though a possible solution is to use a rig with replaceable static mixer elements for testing different reaction schemes. However, this would add to the cost and complexity of the equipment. If turbulent flow conditions are needed, the flow rate would be such that impracticably large amounts of feed would be consumed when running for even a short period.

The micro-channel reactor has been discussed by Ramshaw (1999) as a means of operating laboratory reactions. The basis of this design is that scale-up would be approached by adding more channels of the same dimensions in parallel so that the conditions achieved in small scale operation are identical to those at larger scale

production. Use of the microchannel laboratory scale reactor would not allow comparison to any type of reactor other than the microchannel, as a range of mixing conditions could not be produced. Application to situations where solids or very viscous materials are present would also be prevented. Therefore, the microchannel reactor is not considered as suitable for the protocol approach.

Stirred vessels can provide a wide range of characteristic mixing timescales by varying the feed rate of a semi-batch additive and turbulent energy dissipation rate (see Section 2.5). Operation is subject to very inhomogeneous mixing within the vessel, where mixing energy in the impeller zone can be orders of magnitude higher than at the surface. A major benefit of the stirred vessel is that it is a highly versatile piece of equipment with the ability to cope with different process phases, and as a result is widely used and well understood in the chemicals industry.

Of the laboratory techniques identified above, semi-batch addition into a stirred vessel holds the greatest potential for versatility and ability to produce a wide range of operating conditions. A stirred vessel provides a simple experimental set up and does not consume the large amounts of feed a continuous plant would. However, the vessel would have to be designed to achieve a uniform mixing intensity throughout the vessel. No previous references to using semi-batch addition in stirred vessels to model continuous operation attempts have been discovered in literature, a fact which was confirmed by Bourne (1999).

For performance in static mixers to be modelled through the use of stirred vessels, the mixing environment to which the feed is subject must be equivalent for the two operations. In static mixers, feed is added continuously in stoichiometric amounts. In semi-batch addition to stirred vessels, the feed is added continuously over a period of time, but can be considered to be discretised into small droplets. The discrete drop added at the start will experience a much higher bulk to additive concentration ratio than occurs at any time in static mixer operation. As semi-batch addition and reaction progresses, the concentration of bulk reactant in the vessel will fall, so the ratio to the

additive will also fall to a value comparable to that in the static mixer and then drop below this. Overall, the mean concentration ratio could be considered as equivalent to static mixer operation when taken over the entire feed volume and mixing timescale, though this will have to be considered in more detail in the future.

5.4 PRELIMINARY STIRRED VESSEL PERFORMANCE INVESTIGATION

Performance of existing laboratory stirred vessels has been evaluated to determine the range of conditions these are capable of producing. The intention was to demonstrate whether an existing vessel could be utilised in the protocol and, should a new vessel be required, highlight the aspects of design for attention to be focused upon. The following equipment was used for the investigation.

1) 500 ml conical flask mixed by swirling with the hand
2) Magnetic 'flea' stirrer in a 500 ml conical flask. A flea is a 3cm long and 0.4cm diameter cylinder which is rotated through the use of a rotating magnetic field. Mixer speed is unknown, though the maximum setting was used.
3) Impeller operation at 2000 rpm in a 100mm diameter unbaffled beaker.
4) Impeller operation at 2000 rpm in a 100mm beaker with four 7mm wide baffles.

The impeller used for the tests was a 45mm diameter 4-blade pitched blade turbine of 30° pitch, with blade length = 15mm, width = 7mm and thickness = 2mm. Performance of the above equipment items was tested using the azo-coupling reaction scheme. Diazotised sulfanilic acid of initial concentration of $C_{BO} = 2.55$ mol/m^3 in water was used. A single solution of both 1- and 2-naphthol in water, termed A and C respectively, was prepared with $C_{AO} = 0.0536$ mol/m^3 and $C_{CO} = 0.2142$ mol/m^3. 4 ml of B was added to 200ml of the A and C solution. Appendix B describes the reaction scheme and procedures for determining the turbulent energy dissipation rate from the experimental results.

B was added over a period of approximately 50 seconds to the surface of the liquid in all cases. Values of by-product yield, X_Q, are listed in Table 5.1, alongside the determined turbulent energy dissipation rate, ϵ. A large amount of air was noted to be entrained when mixing with an impeller, which is undesirable as the air will reduce the power input into the liquid for mixing.

Table 5.1 Results of preliminary stirred vessel experiments

Mixing equipment	X_Q	ϵ (W/kg)
Hand	0.559	0.14
Magnetic flea	0.517	0.3
Impeller	0.410	1.3
Baffled impeller	0.407	1.4

The most vigorous mixing provided the highest turbulent energy dissipation rates and therefore the lowest by-product yield. Using baffles in a vessel improves the mixing performance as swirling is reduced and more of the energy input is converted into turbulent energy dissipation. The actual magnitude of ϵ was lower than expected, particularly for the high speed impeller tests, where a value an order of magnitude greater was anticipated.

It is likely that the feed addition time used, 50 seconds, was shorter than the critical feed time of the vessel (Section 2.5.3). This is in comparison to published results, for example Bourne *et al* (1992) where critical feed times of hundreds of seconds are common. The combined effects of addition below the critical feed time, addition onto the liquid surface where the turbulent energy dissipation rate tends to be lower than in the impeller region, and the air entrainment could have caused the low inferred turbulent energy dissipation rates.

These experiments show the limitations of standard laboratory equipment. Hand-swirling may only be used in the most basic experiments, but product quality can be

vastly different from that achieved in more intensely mixed equipment. The magnetic flea mixer is not capable of generating high turbulent energy dissipation or homogenous flow throughout a vessel. Unbaffled vessels suffer from swirling, meaning that not all of the energy input goes into mixing. Baffles prevent swirling, but can result in significant air entrainment at the higher speeds that are required to produce the high turbulent energy dissipation rates experienced within PI equipment. All of these factors demonstrate the need for a new laboratory protocol vessel design.

5.5 PROTOCOL VESSEL DESIGN

For the protocol equipment to be successful at matching the conditions experienced within a static mixer, the following major considerations have to be met:

1) Provide turbulent energy dissipation rates comparable to a static mixer
2) Homogenous mixing throughout the vessel volume
3) Minimise air entrainment

The resulting vessel design is illustrated in Figure 5.2. To provide high turbulent energy dissipation rates, a small volume is preferred as the mixing energy input is then applied to a lower mass of liquid. A 125W laboratory mixer with variable speeds of up to 2650 rpm was available for the experiments. The static mixer experiments being used to benchmark the protocol experiments operated up to a maximum turbulent energy dissipation rate of 118 W/kg. This suggests that an appropriate volume of contents for the protocol vessel is 1 litre with a mass of 1kg, which would supply 125 W/kg input at the maximum mixer speed. To allow a margin of over design and ensure that the target energy input was achieved, a vessel of 10cm diameter and height was selected, providing a volume of 785ml and allowing turbulent energy dissipation rates of up to 150 W/kg. Should much higher energy dissipation rates be required for future experiments, reducing the diameter and height to 8cm would approximately halve the volume and double the maximum turbulent energy dissipation rate for the same mixer.

The perspex vessel had a flat bottom with four 1cm baffles running the full height of the vessel to prevent swirling. To prevent air entrainment, a flat lid was employed. Holes were provided in the lid to allow entry of the impeller shaft and feed pipe. To stop air being drawn down through the mixer shaft hole, and allow additional volume for an additive, a 4cm diameter chimney was fitted onto the lid around the impeller shaft entry hole. Testing of the vessel found that a liquid depth of 1cm in the chimney prevented any air entrainment with the experimental mixer running at its maximum speed. The presence of the chimney will affect the performance of the beaker as a small proportion of the overall vessel, between 1 and 2%, will not be subject to the same turbulent energy dissipation as the bulk liquid. However, this is not expected to introduce a significant error into the experimental results. An additional chimney, with a hole wide enough only for the feed pipe, was been included to allow feed addition through the full depth of the vessel just outside the impeller swept area.

Impeller selection and arrangement were based upon the requirement for homogenous mixing combined with high power input. A pitched blade turbine (PBT) was selected as this is an axial flow impeller and will distribute mixing power input more evenly throughout the vessel than a radial flow impeller, such as the Rushton turbine. Mixing homogeneity can be improved through the use of dual impellers, so two 3-blade PBTs were utilised, spaced equally along the impeller shaft. Relatively large diameter impellers, D=6cm, were chosen as this provides high power input at a given mixer speed (proportional to D^5, Equation 2.1) and more homogenous energy dissipation than smaller impellers. Blade length was 23mm, width is 11mm and thickness 3mm, with blade pitch of 45°. Mixer speed was determined using a stroboscope, which was found to be a more accurate means of determining speed compared to a hand-held tachometer.

Power number of the dual impeller system was measured using a torque meter. Power number is constant in the turbulent regime when Reynolds number, Re, is greater that approximately 10000 (Coulson and Richardson, 1990). Re for a stirred vessel is determined from Equation 5.1, where ρ is the density of the fluid, N is the mixer speed, D the impeller diameter and μ the fluid viscosity. At 780 rpm, where Re = 52500, the

power number was found to be 1.8.

$$Re = \frac{\rho N D^2}{\mu} \tag{5.1}$$

A collar in the vessel base prevented sideways movement of the shaft at the highest rotational speeds. The vessel was secured within a water bath with the mass of water in the bath preventing excessive vibrations at high speeds. There was no temperature control on the beaker and heat transfer through the vessel's perspex walls was minimal. As a result, the temperature within the vessel will increase if it is operated over long periods of time due to the mixing energy being converted into heat. Rate of temperature rise at various speeds, with water as the mixing medium, was measured and is presented in Table 5.2.

Table 5.2 Temperature rise in the protocol vessel

Mixer speed (rpm)	rate of temperature rise (°C/min)
540	0.08
810	0.12
1240	0.41
2000	0.81
2380	1.34

At lower mixer speeds the rate of temperature rise is insignificant, and operating for short periods of time at any mixer speed will not result in an appreciable temperature rise. However, operating over a period of a few minutes at higher speeds may affect the reaction product distribution. A rule of thumb states that reaction rates double with every 10°C rise in temperature. This 10°C rise would occur in little over five minutes of operation at the highest speed and could therefore affect the results of any experiments run over this timescale. Temperature rise effect is considered in Section 5.8.4.

Accurate and smooth addition of feed was required for the experiments. The volumes of liquid added were of the order of 5ml over periods of up to hundreds of seconds. The system chosen for the protocol equipment was addition via a burette, with the prime motivation being simplicity. Total feed volume could be added to ±0.025ml. Feed addition was relatively smooth, though some problems were experienced when feeding over longer timescales when the feed rate tended to drop over time. However, it is shown later that the shorter feed timescales are the most important and burette addition could satisfactorily provide these. Addition time could not be accurately predetermined, but was timed with a stopwatch during the addition.

5.6 PROTOCOL VESSEL CHARACTERISATION

This section describes the characterisation of the vessel to determine the level of mixing that it was capable of producing and the homogeneity of mixing throughout the vessel volume. Performance could then be tested against predictions from mixing correlations. A reaction scheme that provides a wide range of X_Q over the anticipated mixing conditions was selected to reduce experimental error.

5.6.1 Reaction Scheme Selection

The azo-coupling reaction scheme used previously in Section 5.4, where $C_{BO} = 2.55$ mol/m^3, shows very little variation in X_Q of only 0.02 over the 50 to 150 W/kg range. The variation should be as high as possible to reduce the effects of experimental errors on the results. Increasing the concentrations to C_{BO}=30 mol/m^3, $C_{AO} = 0.229$ mol/m^3 and $C_{CO} = 0.917$ mol/m^3 with an addition ratio of 196 (4ml added to 785 ml in the vessel) provides a difference of 0.07 in X_Q over the 50 to 150 W/kg operating range. A characteristic mixing-sensitivity curve for the above concentrations can be generated utilising the mixing models and computer program described in Appendix B. The curve for the above reaction scheme is shown in Figure 5.3 and compared alongside the curve for the lower concentration of $C_{BO} = 2.55$ mol/m^3.

5.6.2 Mixing Homogeneity

Homogeneity of mixing over the depth of the vessel was tested. The feed position was varied at 1cm intervals between the surface and base of vessel using a feed pipe with inner diameter of 1mm, a fixed feed time of eight seconds and mixer speed of 2000rpm. Feed time of eight seconds was below the critical feed time of the vessel, which was later estimated to be approximately 80 seconds. Therefore, the product distributions obtained are mesomixing limited and cannot be used to quantify the turbulent energy dissipation rates within the vessel as this requires micromixing control. However, the results are still comparative for the purpose of examining mixing uniformity.

The results are displayed in Figure 5.4, with the experimentally determined turbulent energy dissipation rate at each location divided by the mean turbulent energy dissipation rate throughout the vessel. The results show that in the impeller regions, the relative turbulent energy dissipation rate is higher than average value of 1.0. At the bottom of the vessel the turbulent energy dissipation rate is below average, whilst in between the impellers the turbulent energy dissipation rate is average. The largest variation is around eightfold between the base of the vessel and the upper impeller region, which is far more uniform than the 50-fold variations Butcher and McGrath (1993) say occur within stirred vessels. Even in static mixers, variations in mixing intensity of 4-fold have been noted by Hearn (1995). Therefore, the protocol vessel design is considered to provide an acceptable uniformity of mixing.

5.6.3 Mixing Efficiency

The turbulent energy dissipation rate within the protocol vessel can be predicted from Equation 2.1 and the vessel design was tested against this correlation. The vessel was operated at a variety of mixer speeds from 500 to 2300 rpm, corresponding to a range of 1-100 W/kg, with feed added between the two impellers at a range of feed times to ensure that micromixing control is achieved. A number of experimental runs were made for each turbulent energy dissipation rate to test repeatability of the results. Each

run utilised a fresh batch of chemicals. Results of the experiments are displayed in Figures 5.5 to 5.10.

Systematic differences can be noted between the different chemical batches. This was possibly caused by errors in the chemical make up. The quantities of chemicals required are very small, in some cases as little as 0.5 grammes, with weighing to ± 0.005g. Experimental errors are discussed further in Section 5.8.2.

A mass balance on the product yield can be calculated to examine the reliability of the results, as described in Appendix B. The mean mass balance for each run is included on each of the figures and is typically ±10%, which is similar to the results found by other workers (see Section 5.8.2).

Most of the experimental results exhibit a smooth feed time curve at lower feed times. At higher feed times, wide scatter can be observed in the by-product yield during individual runs. Potential causes for the scatter could include difficulties in obtaining smooth feeding over longer timescales.

Figures 5.8 and 5.9 for 1800 rpm and 2000 rpm show that the X_Q values increased at longer feed times. This is characteristic of backmixing into the feed pipe, as observed by Baldyga *et al* (1993). Backmixing is where reactants from the vessel move up the feedpipe and reaction occurs here rather than in the vessel itself. This is discussed further below.

Estimating mixing efficiency of the vessel at different speeds depends upon determining the by-product yield, X_Q when micromixing is limiting. For stirred vessels, micromixing control occurs when feed is added above the critical feed time, t_{crit}. It is difficult to pinpoint the critical feed time, but it was determined for Figures 5.5 to 5.10 by inspection. For each of the mixer speeds, values of X_Q were collected for individual chemical batches above the critical feed time. A mean X_Q value was determined for each particular batch and then an overall mean obtained for each mixer speed. No

emphasis was placed on the mass balance of the individual runs. From this mean X_Q, the turbulent energy dissipation rate was obtained using the procedures outlined in Appendix B. For Figures 5.8 and 5.9 where backmixing was causing the values of X_Q to increase, these increasing values were not taken into account in the analysis. The expected X_Q at each turbulent energy dissipation rate can also be predicted through the procedures in Appendix B.

Table 5.3 compares the experimentally determined and predicted X_Q values and turbulent energy dissipation rates.

Table 5.3 Mixing efficiencies at d_p=1mm.

N (rpm)	predicted ϵ (W/kg)	predicted X_Q	experimental X_Q	experimental ϵ (W/kg)	efficiency (%)
500	1.0	0.576	0.511	3.9	379
1000	8.3	0.466	0.444	11.0	133
1500	27.8	0.383	0.381	28.5	102
1800	48.1	0.346	0.341	52.6	109
2000	66.0	0.326	0.343	50.8	77
2300	100.4	0.299	0.321	70.5	70.2

At lower mixer speeds, the experimentally determined turbulent energy dissipation rate was higher than predicted, giving an efficiency of greater than 100%. Potential causes of this are discussed in Section 5.8.3. At higher speeds, the determined mixing efficiency fell below the predicted values, with a possible explanation being the effect of backmixing into the feed pipe. Jo *et al* (1995) have determined the following correlation to prevent backmixing when feeding above a 3-bladed HE-3 axial flow impeller:

$$u_f > 0.15\,u_t \qquad (5.2)$$

u_f is the velocity of the feed stream exiting the feed pipe and u_t is the impeller tip speed.

Assuming this correlation also applies to the 3-bladed axial flow PBT in the protocol vessel, the onset of backmixing can be predicted for the 1mm diameter feed pipe. Table 5.4 shows these calculated values, along with a comparison to a feed pipe with a smaller diameter of 0.5mm. At the highest mixer speed, any feed time above five seconds may be subject to backmixing with a 1mm diameter feed pipe, whereas with a 0.5mm diameter feed pipe, this timescale is nineteen seconds. It is therefore possible that backmixing, which will become more pronounced at longer feedtimes, was causing the apparent decreased efficiency of the vessel at the higher mixing speeds.

Table 5.4 Time to onset of backmixing into 1mm and 0.5mm diameter feed pipes

N (rpm)	1mm (s)	0.5mm (s)
500	21	87
1000	11	43
1500	7	28
1800	6	24
2000	6	21
2300	5	19

When feeding above 30 seconds, the temperature rise within the vessel may begin to affect the results. Higher temperatures will favour the slower, by-product reaction in the azo-coupling scheme as the faster reactions are mixing, not kinetically, limited. Therefore, higher temperatures could also contribute towards the observed increase in X_Q values at longer feed times.

A 0.5mm feed pipe diameter was tested in the vessel at 1800-2300 rpm to examine any improvements in performance this may produce. These results are plotted on Figures 5.11 to 5.13. A wide spread of results is displayed, particularly for 2300 rpm (Figure 5.13), though the mass balances that were calculated are as consistent as the previous

experimental runs. The micromixing controlled values of X_Q for each run and the average value were obtained above the estimated critical feed time. The experimentally determined results are compared to the predicted results in Table 5.5 below.

Experimental efficiencies are approximately 100%, suggesting that backmixing into the feed pipe is greatly reduced when using a smaller diameter feed pipe. Consequently, the 0.5mm diameter feed pipe was used for all subsequent experiments. Reduction in X_Q when using a smaller diameter feed pipe also suggests that backmixing is more significant than the effects of increasing temperature over longer operating periods. Mixing efficiency results are plotted in Figure 5.14, and replotted as mixer speed, N, versus actual turbulent energy dissipation rate, ϵ, in Figure 5.15.

Table 5.5 Mixing efficiencies with $d_p = 0.5$mm

N (rpm)	predicted ϵ (W/kg)	predicted X_Q	experimental X_Q	experimental ϵ (W/kg)	efficiency (%)
1800	48.1	0.346	0.345	49.2	102
2000	66.0	0.326	0.324	68.0	103
2300	100.4	0.299	0.297	103.4	103

5.7 STATIC MIXER EXPERIMENTAL COMPARISON

5.7.1 Introduction

The following experiments were concerned with prediction of the performance of a static mixer through the use of a stirred vessel. The approach required is to achieve the same turbulent energy dissipation rate and then match the mixing mechanism timescales, as shown in Figure 5.16, taking into account the effects of self-engulfment in static mixers. There are three levels of mixing: macro-, meso- and micromixing, of which meso- and micromixing are the most relevant to reactive mixing with fast

kinetics. Correlations for estimating of the timescales for each of these mechanisms are given in Section 2.5.2, with the controlling mixing mechanism being the one with the longest timescale.

Static mixers are subject to self-engulfment, which does not occur in stirred vessels (see Section 2.5.3). Self-engulfment is where the reaction zone fills the entire available volume and then engulfs itself, increasing by-product yield. This means that even if a stirred vessel is run with the same mixing timescales as a static mixer, a lower by-product yield, X_Q, may occur. To achieve similar X_Q values, the protocol vessel feed time would have to be reduced, resulting in longer mesomixing timescales for the vessel than for the static mixer.

Experimental data is available on the operation of a 32mm diameter SMXL-type static mixer (Wadley, 1996) to allow direct comparison of the protocol's results and operation in a static mixer. Flow rates of 0.5, 0.75, 1.0 and 1.25 litres per second produce 7.6, 25.7, 60.8 and 117.8 W/kg. Only four experimental points are available, though this is sufficient for the purposes of this work which is a preliminary investigation into the laboratory protocol concept and procedures.

5.7.2 Experimental Methodology

The characterisation of the experimental vessel found that the apparent efficiency at lower impeller speeds was greater than 100%. The lower two mixing turbulent energy dissipation rates are within this range, so adjustments were made to the impeller speed in an attempt to match the actual turbulent energy dissipation rate using Figure 5.15. From this curve it was estimated that 7.6 W/kg would be produced at 700 rpm, rather than the 972 rpm if 100% efficiency was achieved. 25.7 W/kg was estimated to occur at 1375 rpm rather than 1460 rpm. The two higher turbulent energy dissipation rates should be achieved at 1945 and 2425 rpm assuming the vessel is 100% efficient at these speeds.

Initial concentrations of $C_{BO} = 2.5$ mol/m^3, $C_{AO} = 0.025$ mol/m^3 and $C_{CO} = 0.10$ mol/m^3 were used, with the flow addition ratio of 150 being equivalent to 5.23ml addition of B to the protocol vessel.

Experiments were run in the protocol vessel for each turbulent energy dissipation rate, with the results shown in Figures 5.17 to 5.20. Mixing efficiency was determined from the X_Q values above the critical feed time in the manner described in Section 5.6.3. These efficiencies are given below in Table 5.6. Comparisons are made between the experimentally obtained turbulent energy dissipation rate and that intended by the experiments, which is the same as the values used in the static mixer tests. This gives the experimental efficiency in Table 5.6 below. The actual efficiencies at the impeller speeds used are also given.

Table 5.6 Mixing efficiencies from the protocol experiments

N (rpm)	desired ϵ (W/kg)	predicted X_Q	experimental X_Q	experimental ϵ (W/kg)	experimental efficiency (%)	actual efficiency (%)
700	7.6	0.197	0.218	4.5	59	161
1375	25.7	0.142	0.158	17.5	68	82
1945	60.8	0.113	0.149	21.2	35	35
2425	117.8	0.097	0.138	30	25	25

It can be seen that the experimental efficiency is much lower than expected in all cases. 700 rpm was expected to produce 7.6 W/kg, but only produced 4.5 W/kg. However, this is still higher than the 3.0 W/kg that should occur at 700 rpm, showing the actual efficiency to be 161%. The next highest speed, 1375 rpm, was expected to produce an efficiency of 120%, though the actual efficiency at this speed is 82% and the efficiency compared to that desired is only 68%. Mixing at higher speeds was assumed to be 100% efficient, but it is shown that this was actually only 35% and 25% efficient.

For the purposes of the experimental analysis it is assumed that the all turbulent energy

dissipation rates are equal to the desired value used in the static mixer experiments. Implications of this assumption and potential causes of the low experimental efficiency are discussed in Section 5.8.3.

5.7.3 Experimental Analysis

The objective of the protocol investigation is to predict the feed time, t_f, for semi-batch addition into stirred vessels that achieves the same product yields as static mixer operation. The feed time at which the X_Q value for the vessel matches the X_Q value achieved in the static mixer are indicated on Figures 5.17 to 5.20 and summarised in Table 5.7.

Table 5.7 Vessel feed time to match static mixer X_Q

ϵ (W/kg)	Static mixer X_Q	t_f to match X_Q (s)
7.6	0.288	14
25.7	0.236	6
60.8	0.196	5
117.8	0.189	3

The controlling mechanism in the static mixer is known to be inertial convective disintegration mesomixing. As all of the vessel feedtimes were below the critical feed time, the vessel was also mesomixing controlled. The mesomixing timescales for the vessel can be estimated by three mesomixing correlations for turbulent dispersion with a point source, turbulent dispersion with a finite source and inertial convective disintegration (Equations 2.7, 2.9 and 2.12 respectively).

The value of L, the turbulence lengthscale in Equations 2.7 and 2.9, was estimated to be 1.2mm. This is approximately 0.52w, where w is the projected height of the impeller blades used in the protocol vessel. This correlation was suggested by Baldyga and

Bourne (1992) for a Rushton turbine, but as there is no information available on other impeller types, it is assumed to apply equally to PBTs.

To determine the mesomixing timescales, it is necessary to know the local fluid velocity, u. The local velocity has been determined by McCabe (1985) as approximately 25% of the impeller tip speed when feeding near a Rushton turbine. However, it is desirable to have a simple correlation that can be used for all impeller types and correlations. The approach decided upon was to use the impeller flow number, fl, as a means of estimating fluid flow velocities. Flow number of an impeller is defined by McCabe (1985) as:

$$fl = \frac{Q_i}{N\ D^3} \tag{5.3}$$

Q_i is the volumetric flow rate of bulk liquid through the impeller. Values for fl can be obtained from literature for different types of impeller. The mean velocity of flow through the impeller is assumed to be Q_i divided by the cross-sectional area of the impeller. This gives:

$$u = \frac{4\ fl\ N\ D}{\pi} \tag{5.4}$$

Inserting the value of flow number for a Rushton turbine as 0.65, estimated from Musgrove (1996), gives a velocity of 26% of the impeller tip speed, which is close to the 25% determined by McCabe (1985). This suggests that the flow number method is indeed a means of estimating local fluid velocity. Impeller flow number for the protocol vessel was estimated to be 0.78, with details of the procedures and references used during the estimation given in Appendix C.

The three mesomixing timescales have been determined for the protocol vessel at the feed times in Table 5.7. These timescales are displayed in Table 5.8 below, alongside

the inertial convective disintegration timescale for the static mixer at all four turbulent energy dissipation rates and the micromixing timescale, which is the same for both systems.

The longest vessel mixing timescale, and hence the controlling mechanism, is turbulent dispersion mesomixing with a point source, t_D, at the required feedtimes. As a result, for all subsequent analysis, turbulent dispersion with a point source will be applied to the vessel and inertial convective disintegration to the static mixer.

Table 5.8 Meso- and micromixing timescales

ϵ (W/kg)	t_f (s)	t_{micro} (s)	static t_S (s)	vessel t_S (s)	vessel t_D (s)	vessel t_{D1} (s)
7.6	14	0.0059	0.0186	0.0080	0.0124	0.0020
25.7	6	0.0032	0.0124	0.0062	0.0129	0.0013
60.8	5	0.0021	0.0093	0.0045	0.0087	0.0010
117.8	3	0.0015	0.0075	0.0040	0.0093	0.0008

Inertial convective disintegration timescales for the static mixer, t_S, were similar to the values of turbulent dispersion timescales of the vessel, t_D, for the same X_Q values. It was anticipated that t_D would be greater than t_S in all cases due to the effects of self-engulfment in static mixer operation, as mentioned above in Section 5.7.1. However, the value of t_D is very dependent upon the value of L used. If L was estimated to be 1mm rather than the 1.2mm applied above, all of the values of L_D would be greater than L_C. This shows that an increased characterisation of the protocol vessel is required to enable more accurate determinations of all the factors involved in the estimation of the mesomixing timescales.

Calculations are available to estimate the effects of self-engulfment (Baldyga & Bourne, 1999, Chapter 8). These calculations are of a relatively complex nature and require knowledge of the reaction kinetics, which are not always available. As a result, it was

decided to investigate the possibility of using a simpler, empirical means of predicting the feed time required to achieve the same X_Q value in the vessel as occurs in the static mixer.

5.7.4 Feed Time Prediction

Comparing t_S for the static mixer and t_D for the vessel in Table 5.8 allowed an empirical factor to be determined that shows the proportionality of the comparative mesomixing timescales. The ratio of t_S to t_D is termed γ (Equation 5.5) and given in Table 5.9.

$$\gamma = \frac{t_S}{t_D} \tag{5.5}$$

Table 5.9 Ratio of mesomixing timescales

ϵ (W/kg)	static t_S (s)	vessel t_D (s)	γ t_S/t_D
7.6	0.0186	0.0124	1.50
25.7	0.0124	0.0129	0.96
60.8	0.0093	0.0087	1.07
117.8	0.0075	0.0093	0.81

The ratio of the static mixer mesomixing timescale to the vessel mesomixing timescale, γ, tended to decrease at the higher turbulent energy dissipation rates, as shown in Figure 5.21. The nature of the trend cannot be fully determined due to the limited experimental data.

Equations 2.7 for t_D can be substituted into Equation 5.5 to give:

$$t_S = \frac{\gamma\ Q_B}{0.124\, n_f\, u\, \epsilon^{1/3} L^{4/3}} \tag{5.6}$$

Q_B for the vessel is equal to V_B, the volume of additive, divided by the feed addition time, t_f. Vessel feed time is the parameter that the protocol is aiming to predict. Therefore, Equation 5.6 can be rearranged to give:

$$t_f = \frac{\gamma \ V_B}{t_S 0.124 \, n_f \, u \, \epsilon^{1/3} L^{4/3}} \qquad (5.7)$$

Fluid velocity, u, and turbulent energy dissipation rate, ϵ, can be substituted by Equations 5.4 and 2.1 respectively. Static mixer mesomixing timescale, t_S, can be determined for a particular static mixer type and flow rate from Equation 2.12.

A similar approach and correlation can be derived for each of the different mesomixing mechanisms depending upon which controls a particular system.

5.7.5 Static Mixer Performance Prediction Procedures

Outline procedures can now be set for using protocol experiments to predict the performance of static mixers, though these are limited to when t_D is the controlling mechanism within the vessel and t_S is the controlling mechanism within the static mixer. These procedures follow those given in Figure 5.16, with the exception of the addition of the γ factor to account for self-engulfment.

When a design of static mixer and flow rates through it are known, the turbulent energy dissipation rate and timescale of the controlling mixing mechanism can be calculated. Operating the protocol vessel at the same turbulent energy dissipation rate and varying feed times will produce a curve of product quality versus feed time. Figure 5.21 is used to estimate a value of the multiplication factor γ at the required turbulent energy dissipation rate. Equation 5.7 then allows the required feedtime to be calculated and the product quality at this feed time read off the curve.

If the static mixer is micromixing controlled, product quality above the critical feed time in the protocol vessel is required.

Identification of a suitable static mixer design can also be achieved through use of the laboratory protocol. A desired product quality should be determined during the chemistry audit section of the methodology along with an indication of the turbulent energy dissipation rate required to achieve this quality. By generating a feed time curve at the appropriate turbulent energy dissipation rate, the feed time required to achieve the desired product quality can be determined. The mixing timescales can be back-calculated from Equation 5.7. This will lead to the sizing and flow rates required through the static mixer to achieve the same mixing timescales. Should the design prove infeasible, for example providing too high a pressure drop, feed time curves can be generated at different turbulent energy dissipation rates until a suitable design is produced.

5.8 DISCUSSION OF EXPERIMENTAL RESULTS

5.8.1 Introduction

A stirred vessel with semi-batch addition has been selected as an appropriate means of operating the laboratory protocol. The turbulent energy dissipation rates generated by the specifically designed vessel was far higher than can be achieved in normal laboratory equipment, with homogeneity of mixing produced by the use of relatively large diameter dual impellers. Performance of the vessel was explored and initial investigations made into whether the protocol approach can be applied to model the performance of static mixers. Issues relating to the reliability of the experimental results are discussed below.

5.8.2 Experimental Errors

The experiments carried out were subject to errors in the operation and analysis, with the small scale of the experiments making small errors more significant. The most significant errors occur from: determining the mixer speed (resulting in ±2% in ϵ);

making up reactants (up to ±1% in weight for the higher concentration experiments and up to ±4% for the lower concentrations); analysis via the spectrophotometer which produces errors of ±0.005 in X_Q, or up to 3%; volume of liquid in the chimney not subject to mixing intensity is up to 2%; feed additive volumes are approximately ± 0.5%.

From these errors, it is realistic to expect the experimental by-product yield X_Q values to be ±10%, a fact which can be seen through the scatter experienced within the same batch and between different runs, shown in Figures 5.5 to 5.13 and 5.17 to 5.20. Mass balances from the experiments indicate a 10% error in the product analysis. Pearce (1998) found the mass balance for azo-coupling reactions was consistently 10% too low, stating that previous workers have also experienced up to 10% differences. One hypothesis reported by Pearce is that errors in the analysis of spectrophotometer data causes errors in the absolute values of dye product obtained. This does not affect the yield values, which are the important ones in analysis of the experimental results.

Experimental make-up and operational procedures should be examined further in the future to try and reduce the errors experienced during laboratory protocol experiments.

5.8.3 Mixing Efficiency Predictions

During testing of the equipment with the azo-coupling reaction scheme of C_{BO}=30mol/m^3, backmixing into the 1mm diameter feedpipe was found to occur. A 0.5mm feed pipe reduced the backmixing effects, indicated by the 100% mixing efficiency achieved at the higher mixing speeds. At lower mixing speeds, the experimentally determined efficiency was higher than expected. Increased apparent efficiency could be caused by the longer feed plume dispersion timescales at lower mixer speeds, meaning the fast reaction is localised around the impellers where the local turbulent energy dissipation rate is higher than the mean value. As mixer speed increases, the faster mixing rates will cause the reaction zone to increase in size and fill a larger proportion of the vessel, therefore exposing the reactants to more uniform

energy dissipation. As a result of these findings, the mixer speeds for the static mixer comparison tests were adjusted, assuming 100% efficiency at the higher speeds, but greater than 100% efficiency at lower speeds.

Use of the lower concentration azo-coupling reaction scheme where C_{BO}=2.5mol/m^3 showed that in all cases the experimentally determined efficiency was lower than that achieved with the higher concentration experiments. One possible explanation of the decrease in efficiency is that lower concentrations are more susceptible to the effects of backmixing. Examination of Figure 5.3 shows that at higher turbulent energy dissipation rates, even a small increase in X_Q can result in a significantly lower determined turbulent energy dissipation rate, therefore decreasing the apparent efficiency. As the curve for lower concentrations in Figure 5.3 is shallower at higher turbulent energy dissipation rates, the same increase in X_Q due to backmixing will decrease the determined turbulent energy dissipation rate far more for lower concentrations than higher concentrations.

Lower than expected efficiencies when C_{BO}=2.5 mol/m^3 suggests that the decision to adjust the mixer speed to account for the greater than 100% efficiencies at lower speed was not correct. However, if backmixing indeed has a greater effect at lower concentrations, then it is not possible to determine the actual mixing efficiency in the vessel and therefore verify or disprove the corrections made. For the purposes of experimental analysis, 100% mixing efficiency was assumed for all speeds. Backmixing has a greater effect at longer feed times when the velocity of fluid exiting the feed pipe is low, so the shorter feed times, where the comparisons to static mixer operation took place, may not be significantly affected and indeed produce 100% efficiency.

Further experiments are required to investigate this in more detail. Experiments should be run with varying concentrations and feed pipe diameters to fully characterise the onset and effects of backmixing.

5.8.4 Temperature Rise Effects

The protocol vessel did not include any heat transfer capability as it was intended to examine only the effects of mixing on a chemical reaction scheme. When operating for longer periods, the vessel temperature can rise appreciably. In experiments run with long feed times, to the order of minutes, it is possible that the temperature will affect the results as the reaction kinetics change with temperature. However, the feed times found to be necessary to match the static mixer productivity in the above experiments are very short, ranging from fourteen seconds at the lower mixer speeds to only three seconds at the higher mixer speeds. As a result, temperature rise should not appreciably affect the most significant results.

5.8.5 Static Mixer Performance Predictions

Anticipated protocol procedures for modelling the performance of PI equipment were identified at the onset of the protocol investigation and are shown in Figure 5.1. These procedures were updated to apply specifically to the modelling of static mixer operation in Figure 5.16. The approach is based upon matching the controlling mechanisms in both the vessel and the static mixer, with the only major difference expected to be due to the effects of self-engulfment in static mixers.

A different mesomixing mechanism was found to be controlling in the static mixer compared with the protocol vessel. Differences in the controlling mechanism timescale for the two systems was accounted for through the use of an empirical multiple, denoted γ. Based upon a limited set of static mixer experimental results, there appears to be a consistent trend between the vessel performance and the static mixer performance. Estimations made in the determination of the mixing timescales mean that all values can only be treated as approximations rather than absolute values.

The empirical approach is very much a first-cut method of comparing the performance of the vessel and static mixer operation. A wider range of testing and comparisons is

required to examine whether the same approach can be applied in all cases, or whether an alternative means of matching static mixer and stirred vessel performance should be developed. This will need static mixer experiments to be run in parallel with protocol vessel experiments, examining the effects of variations in: chemical concentrations; feed pipe diameter; viscosities; reaction schemes; static mixer types; static mixer geometries. Performance of the protocol vessel will also have to be examined in more detail to experimentally determine the impeller flow number and turbulent macro lengthscale for use in estimation of the characteristic mixing timescales.

5.9 SUMMARY

The objective of this chapter was to develop tools and techniques for the laboratory protocol aspects of the PI methodology. The protocol will allow PI reactors to be modelled in the laboratory, thereby increasing the likelihood of it being applied. The potential for simulating continuous, intensified operation in static mixers forms the majority of the investigation. A small scale stirred vessel was selected as the most appropriate protocol equipment, which is the first time that an attempt has been made to use semi-batch addition in stirred vessels to simulate continuous operation. Existing laboratory stirred vessels were shown to be inadequate for the purposes of the protocol, requiring a new design for the protocol vessel.

Performance of the protocol vessel was compared to that of static mixer experiments previously run under the same chemical and mixing conditions. The basis for comparison is to determine the vessel feed time required to produce the same product quality as that achieved in a static mixer. An empirical correlation was produced from the experimental results, though this is an initial approach and will require an extensive experimental study to develop the techniques further. This study cannot be attempted during the timescale of this thesis and is therefore recommended as future work.

Testing of the protocol vessel additionally revealed a number of design aspects that

require further development to increase applicability of the protocol. These are covered in the discussion in Chapter 7, whilst Chapter 6 shows how the protocol fits into the overall methodological approach.

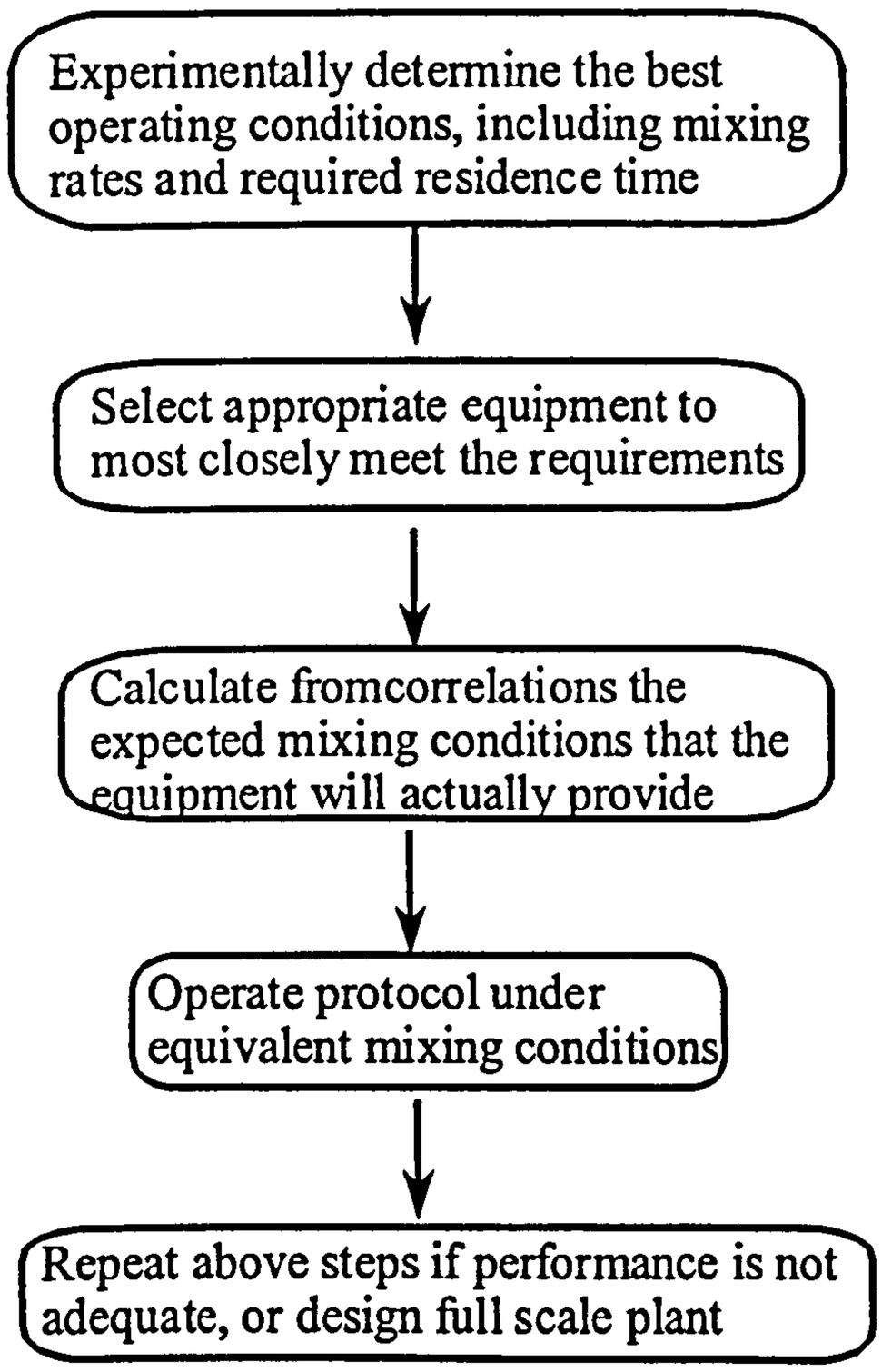


Figure 5.1 Procedures for modelling PI equipment

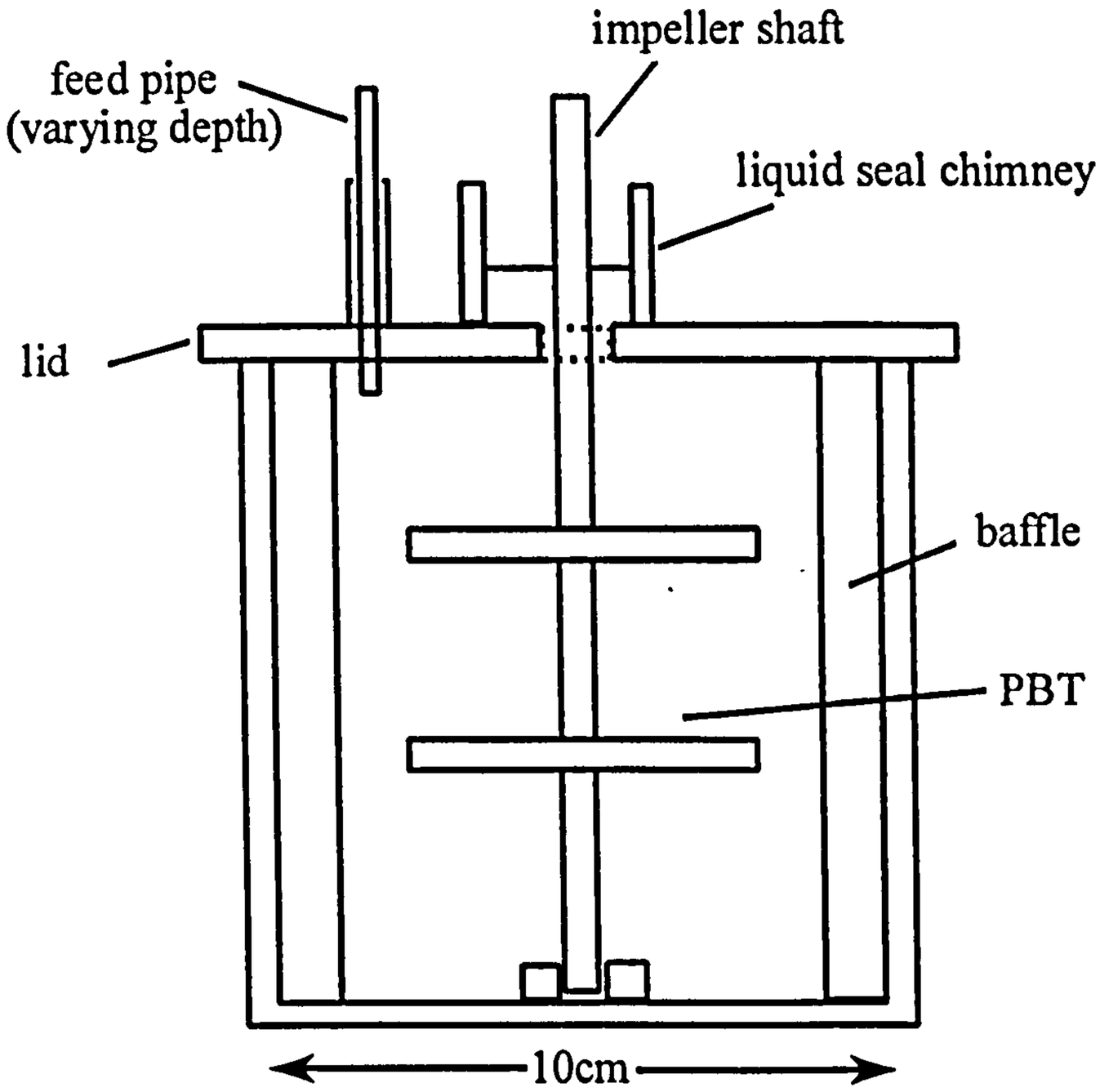


Figure 5.2 Laboratory protocol vessel

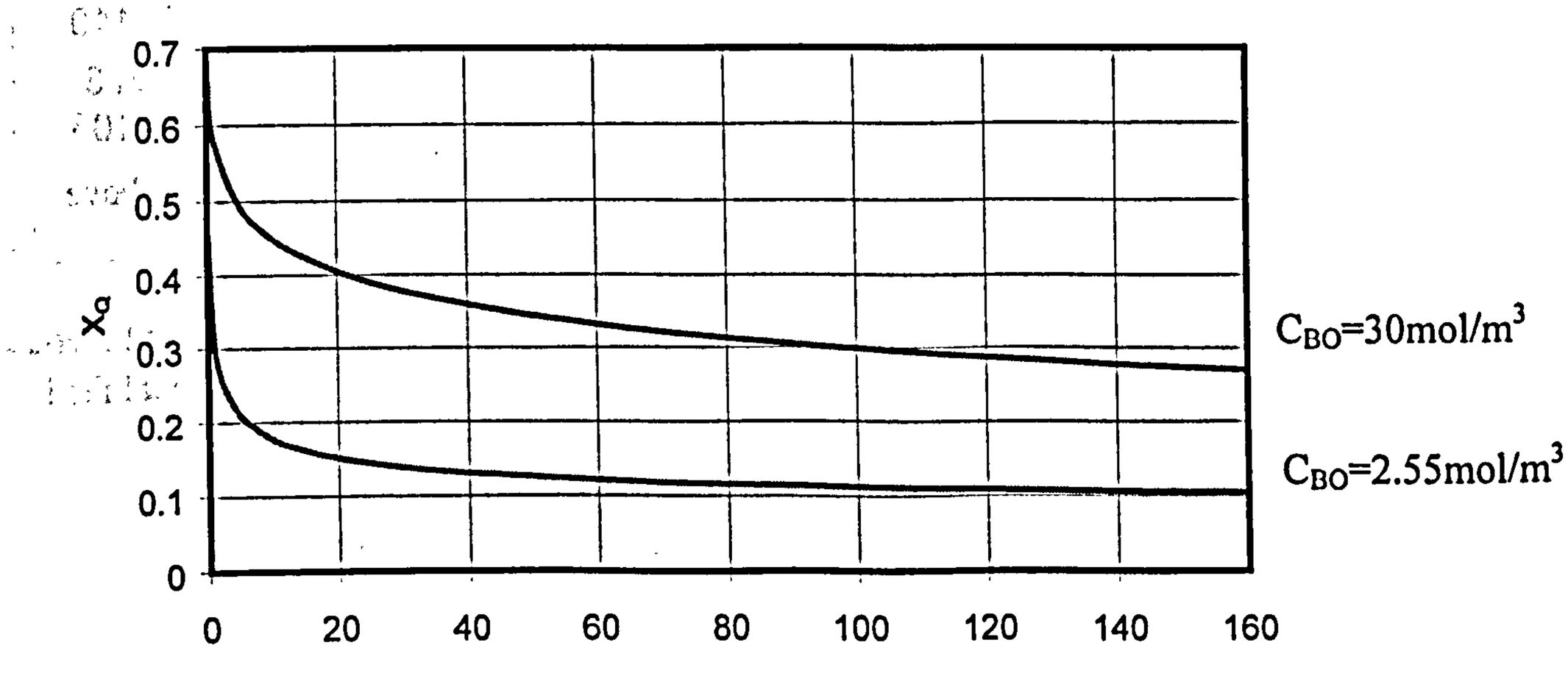


Figure 5.3 Mixing-sensitivity of the test reaction schemes

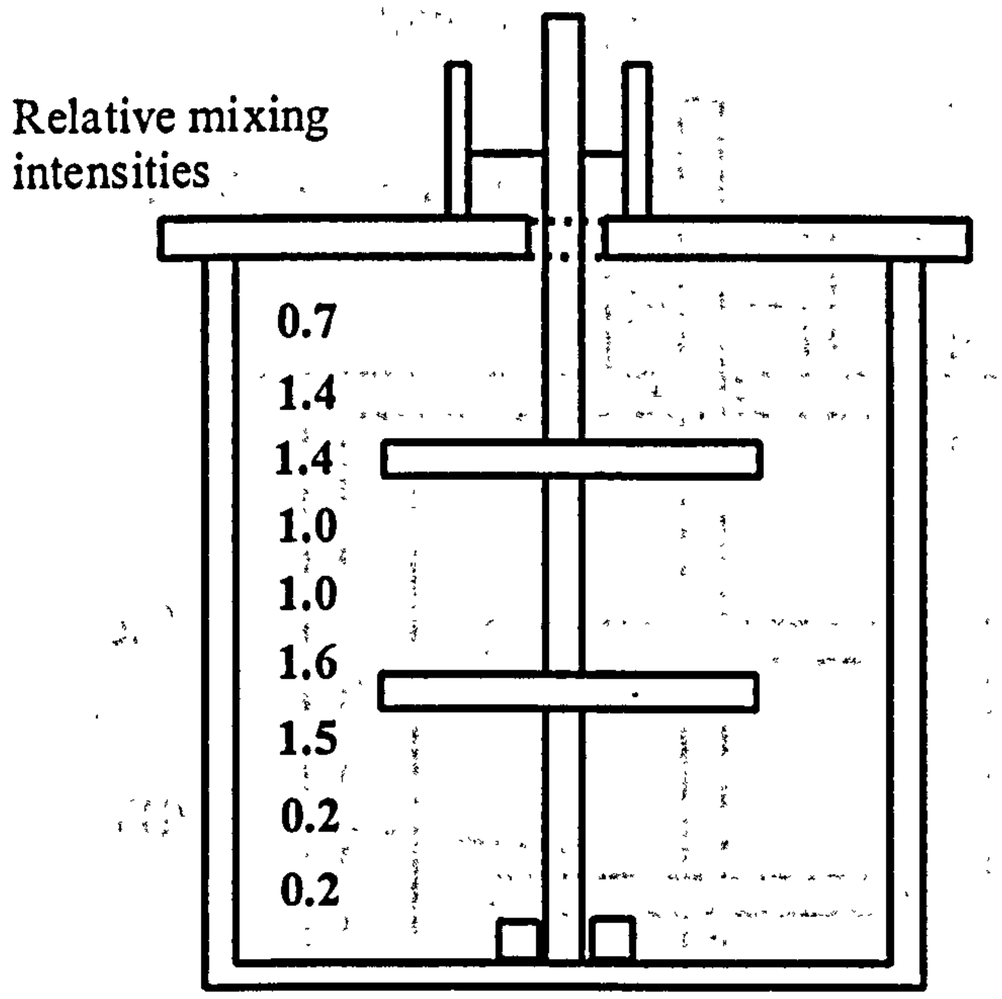


Figure 5.4 Mixing uniformity within the laboratory protocol vessel

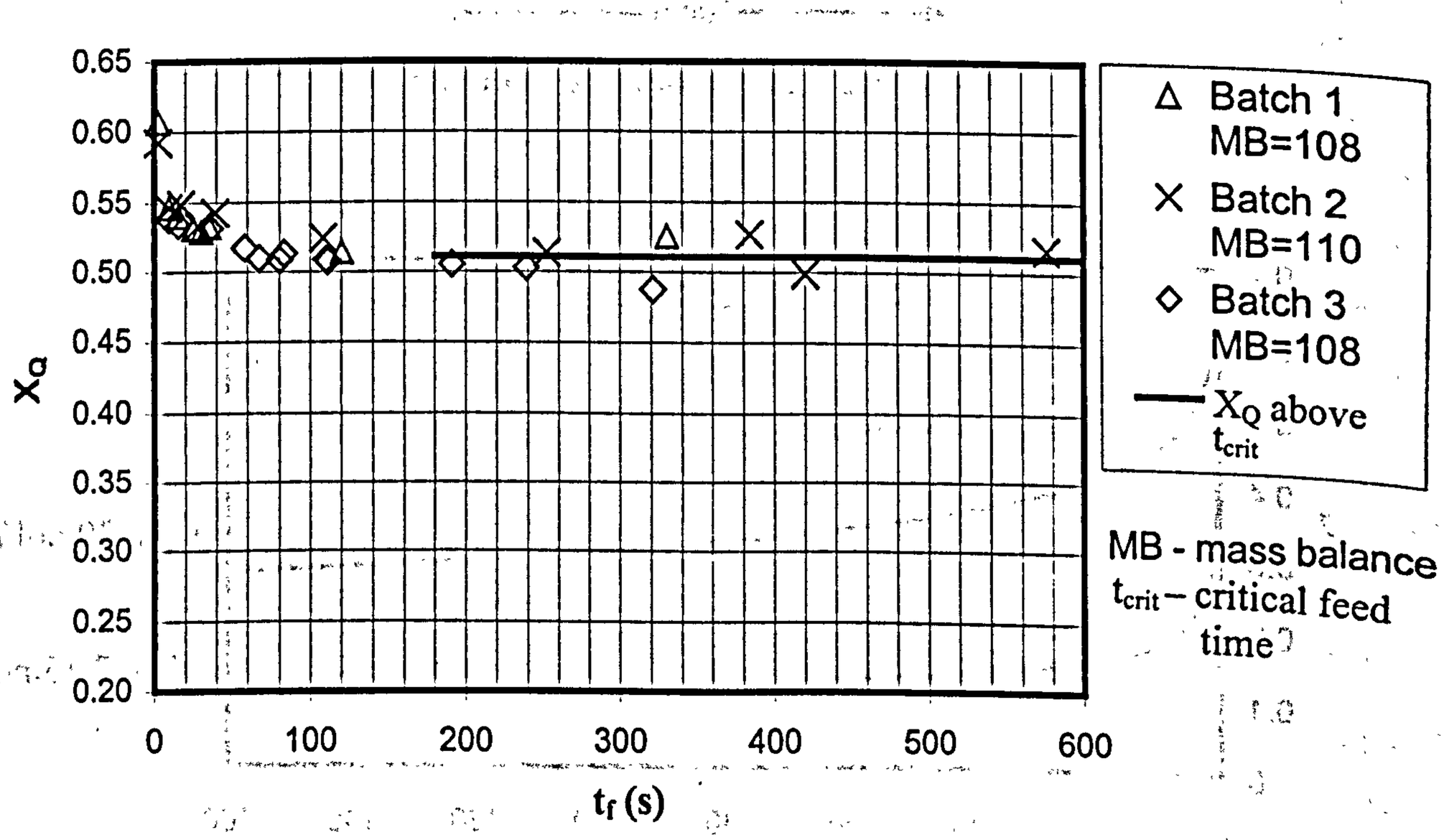


Figure 5.5 Experimental results for C_{BO}=30mol/m^3, N=500rpm, d_p=1mm

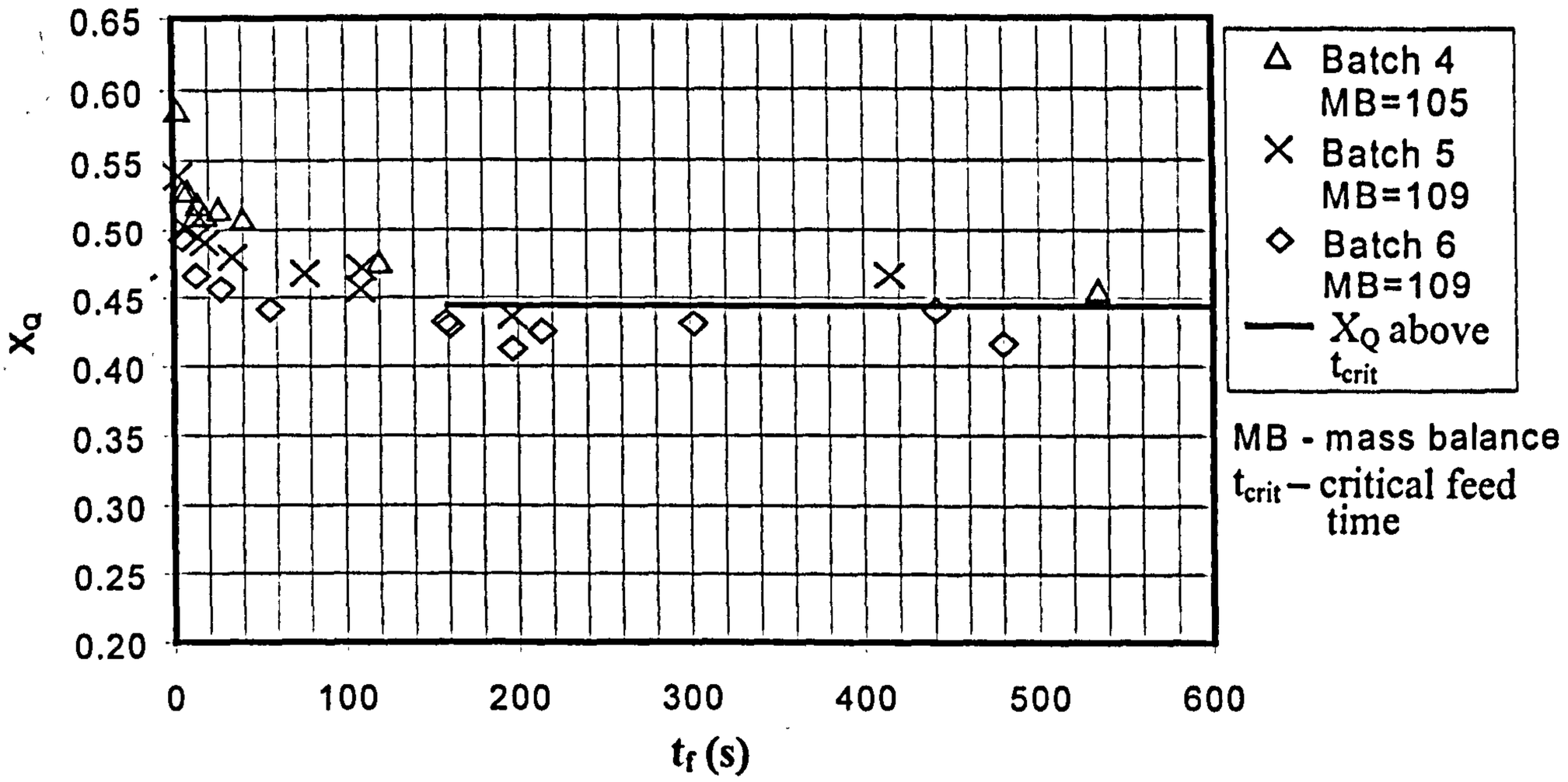


Figure 5.6 Experimental results for C_{BO}=30mol/m^3, N=1000 rpm, d_p=1mm

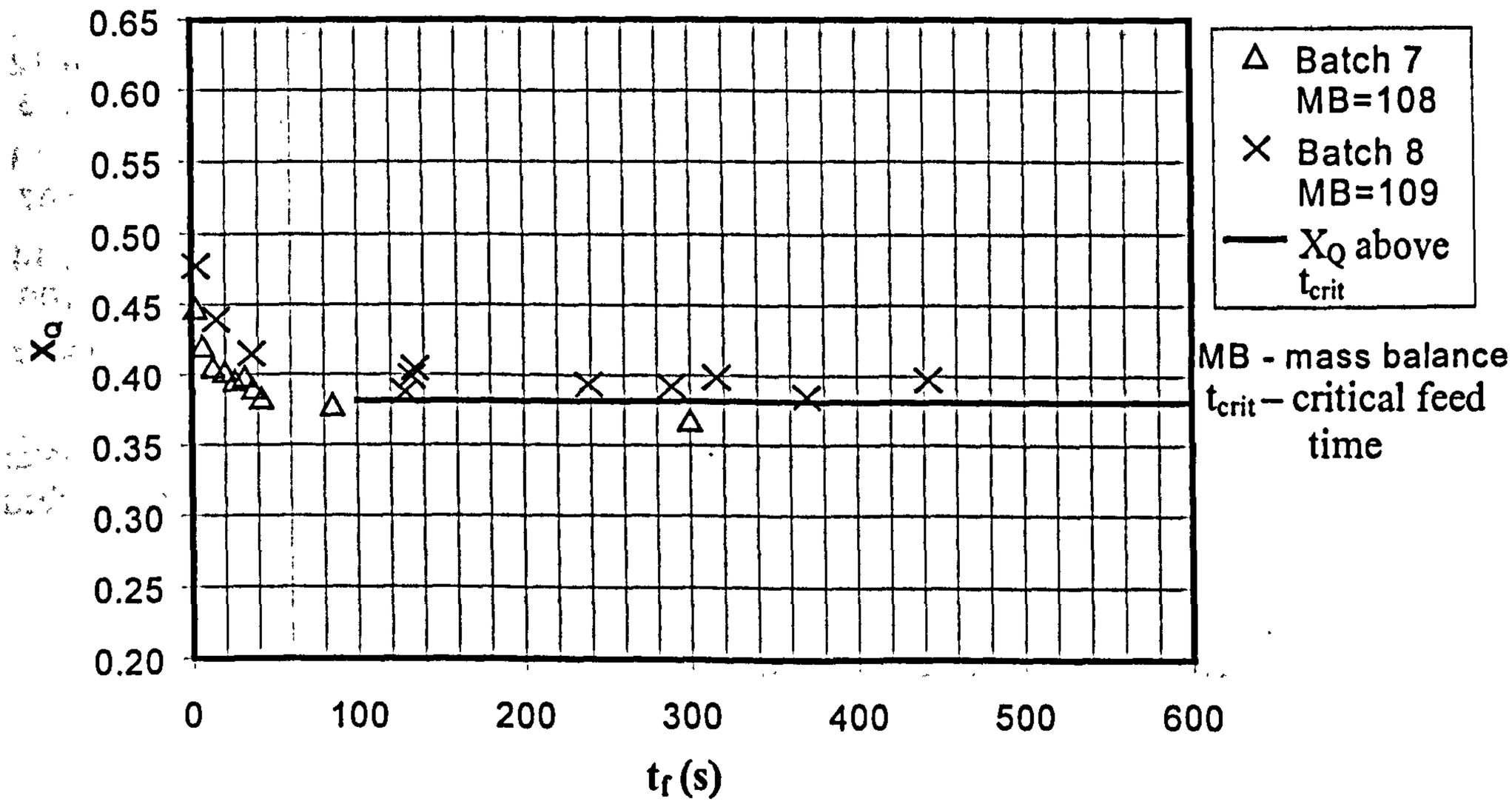


Figure 5.7 Experimental results for C_{BO}=30mol/m^3, N=1500 rpm d_p=1mm

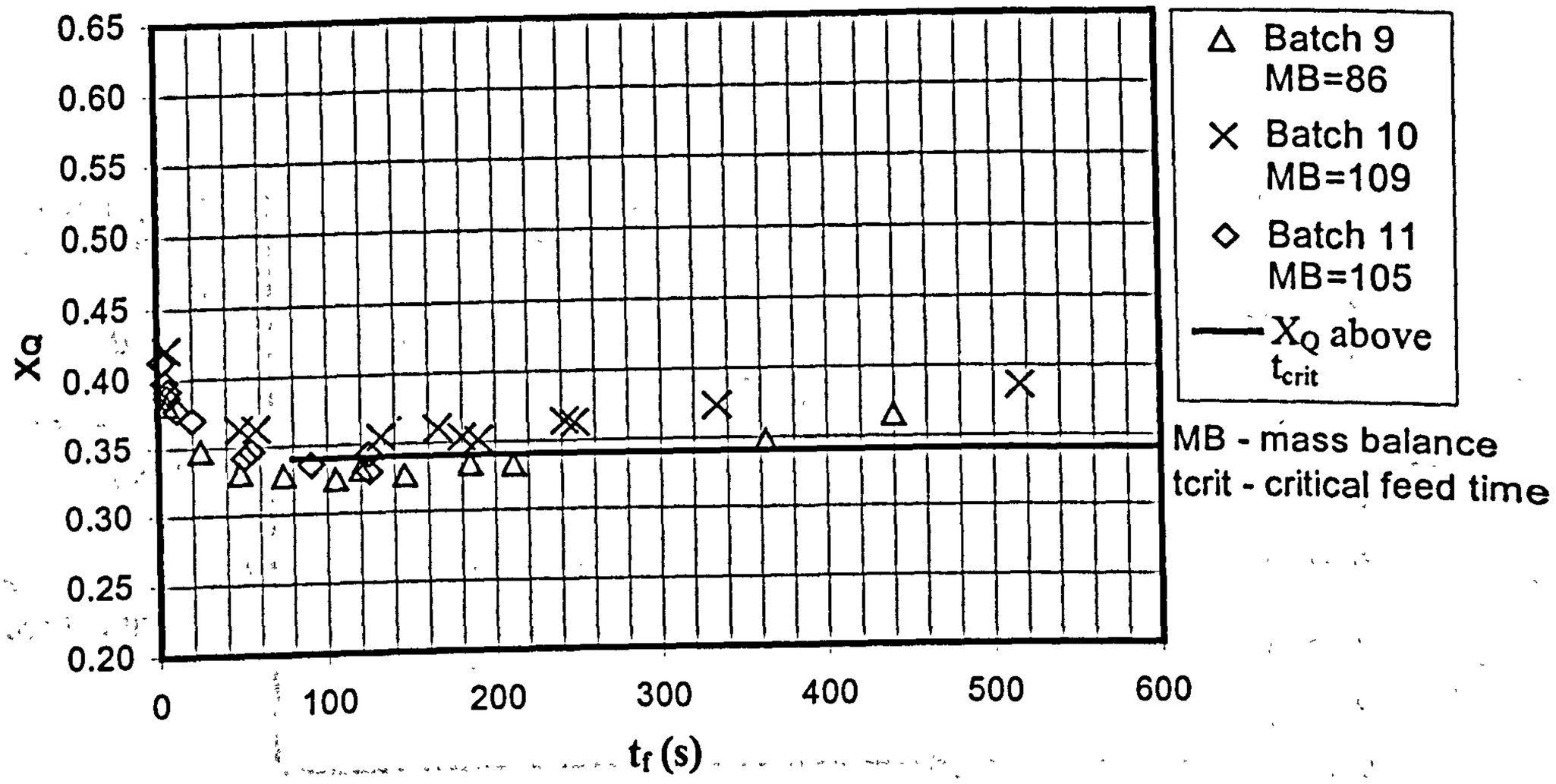


Figure 5.8 Experimental results for C_{BO}=30mol/m^3, N=1800rpm, d_p=1mm

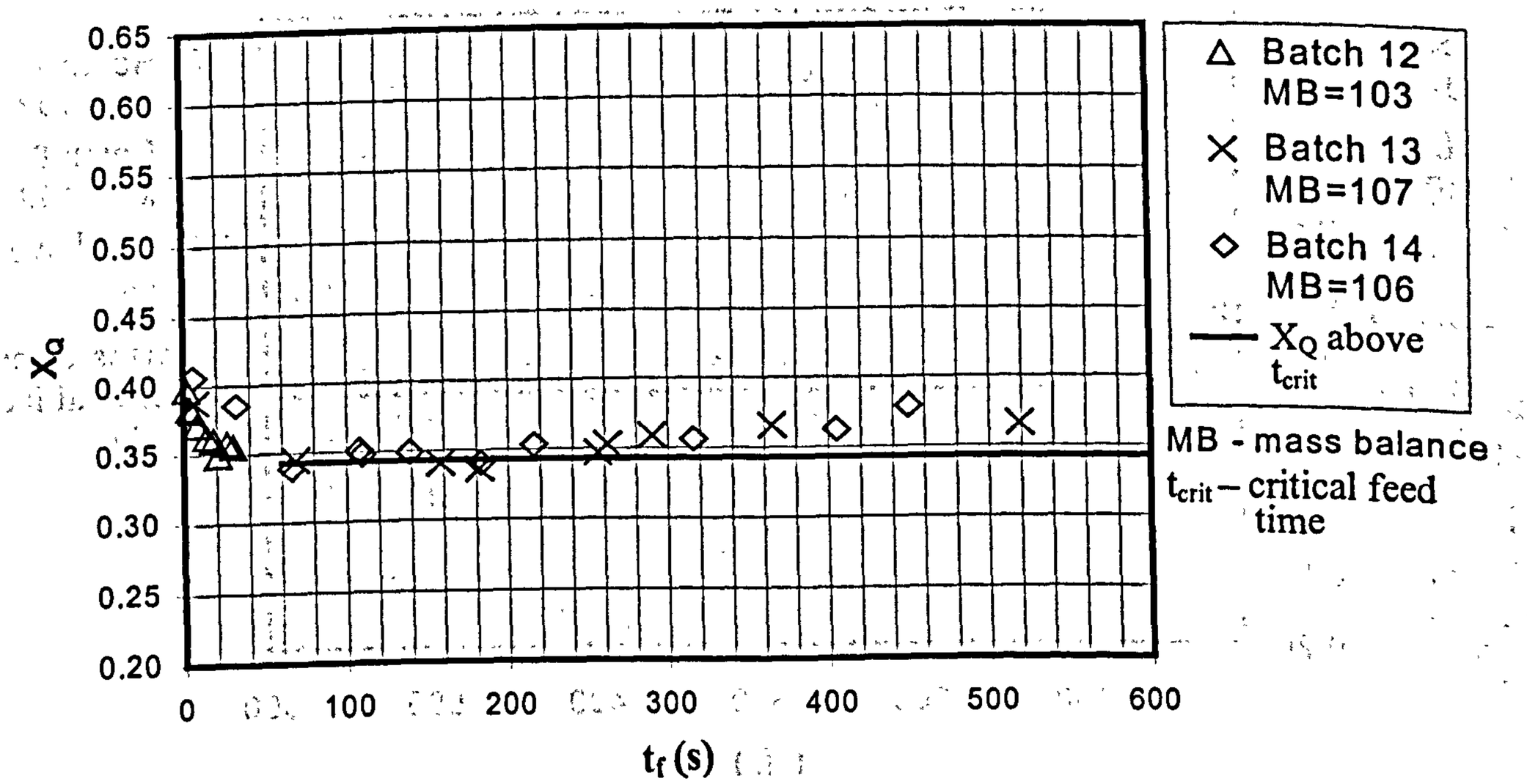


Figure 5.9 Experimental results for C_{BO}=30mol/m^3, N=2000 rpm, d_p=1mm

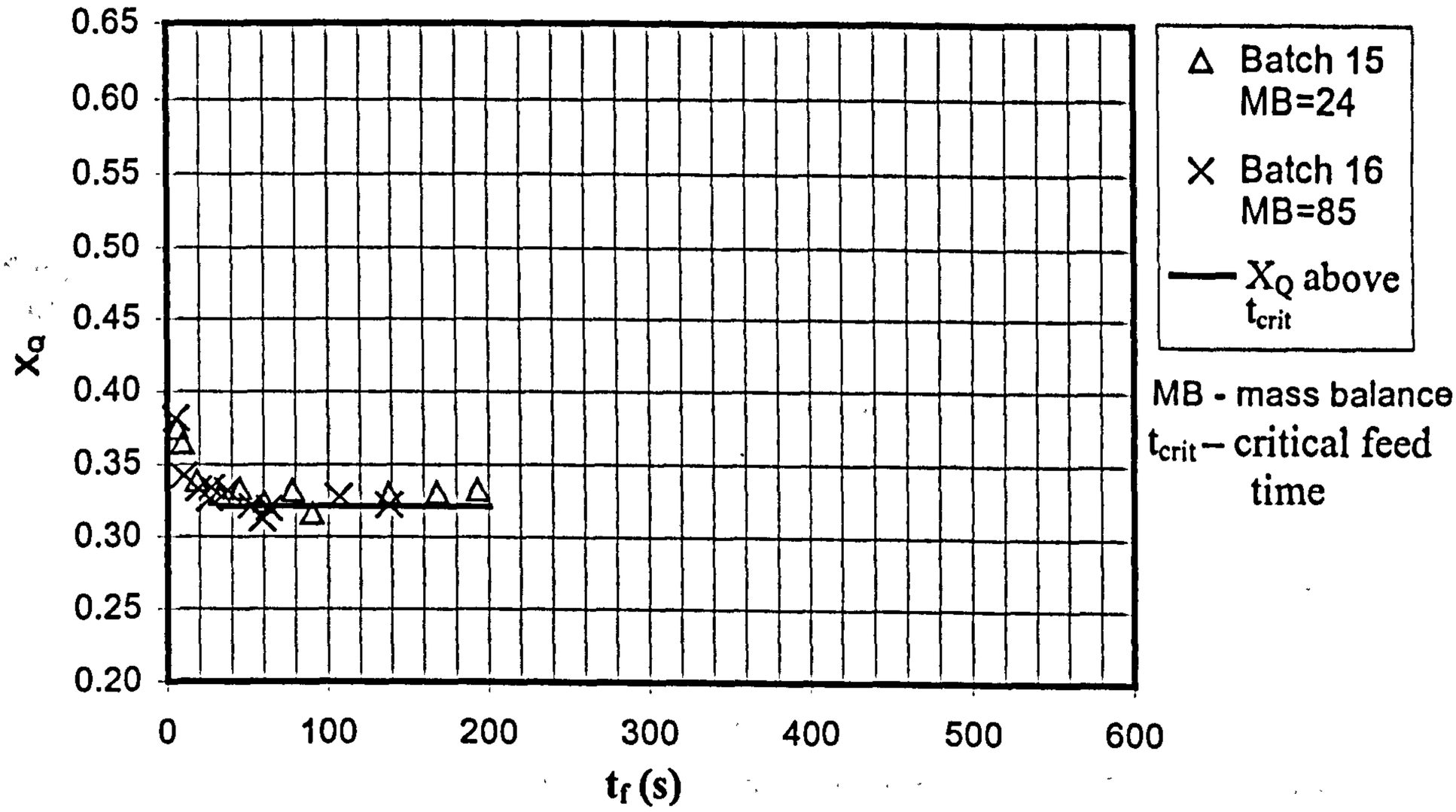


Figure 5.10 Experimental results for C_{BO}=30mol/m^3, N=2300 rpm, d_p=1mm

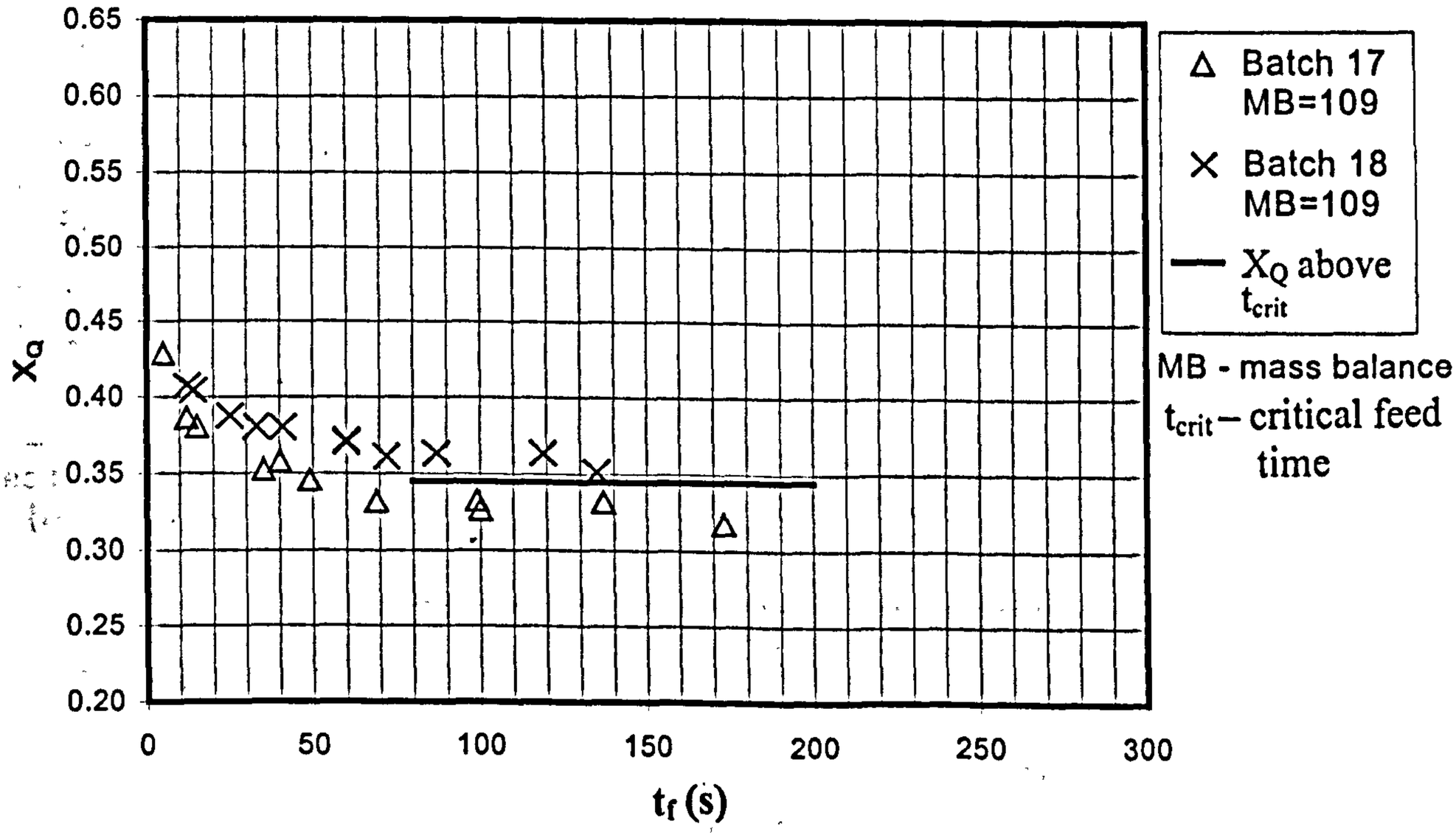


Figure 5.11 Experimental results for C_{BO}=30mol/m^3, N=1800 rpm, d_p=0.5mm

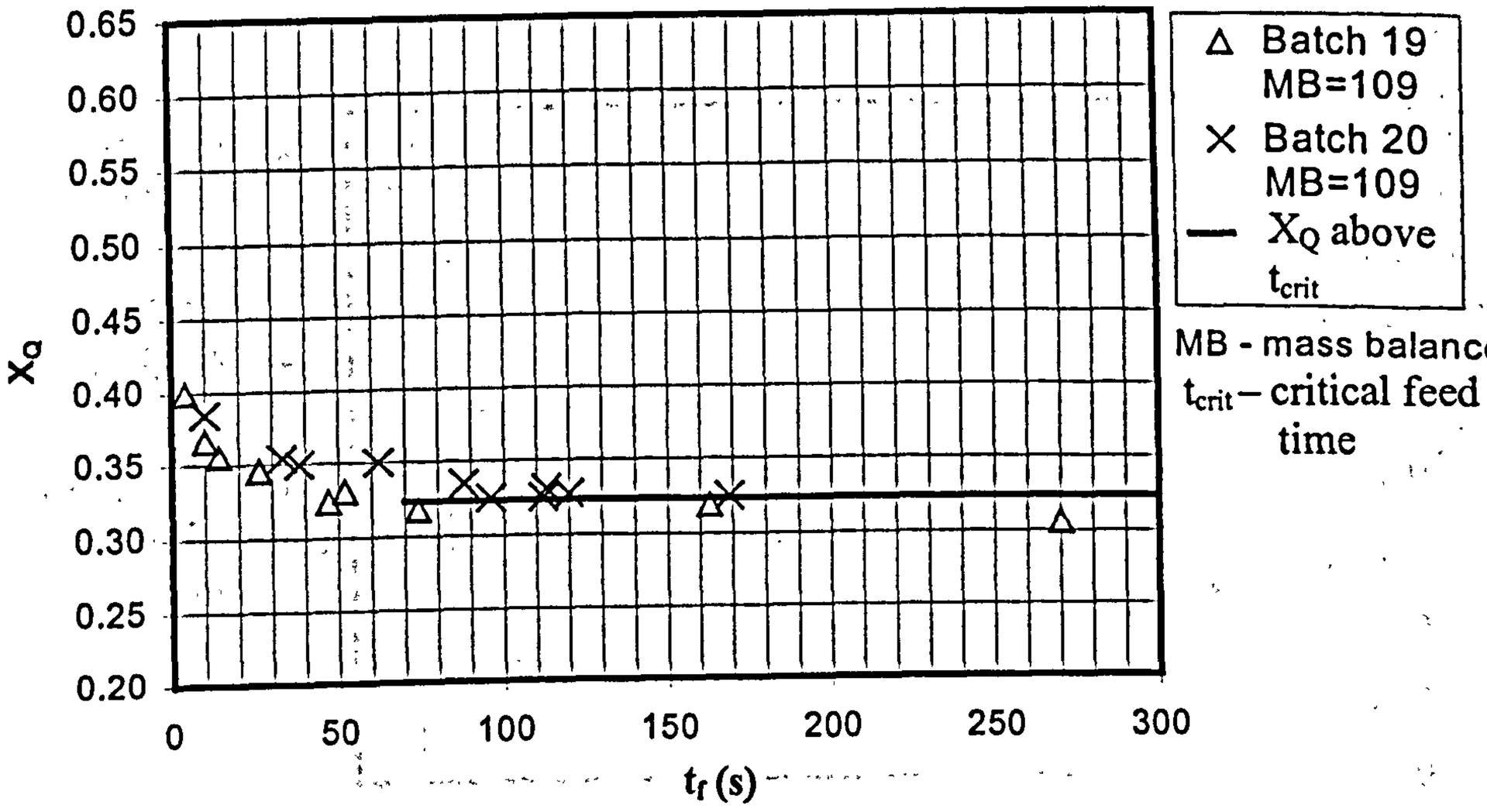


Figure 5.12 Experimental results for C_{BO}=30mol/m^3, N=2000rpm, d_p=0.5mm

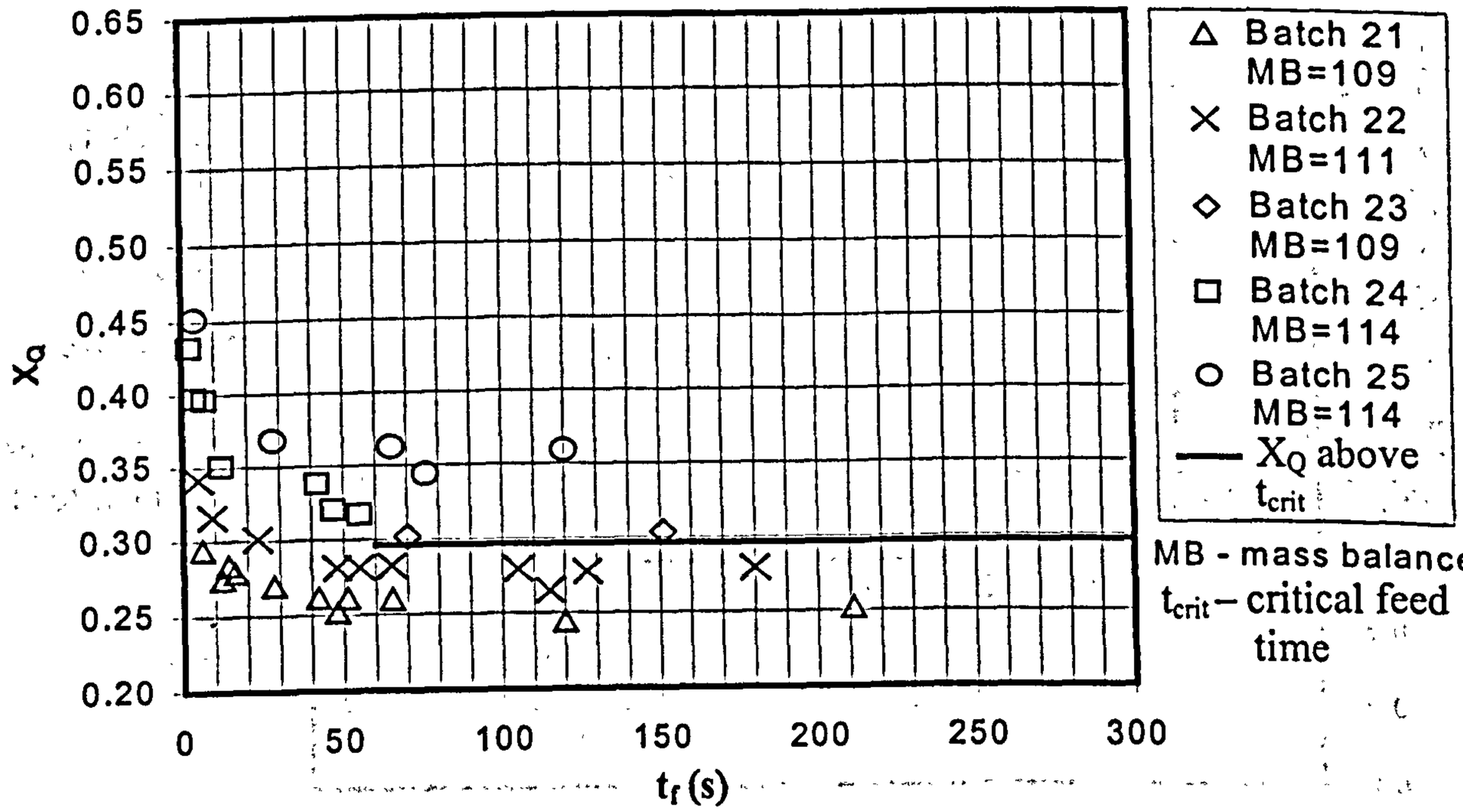


Figure 5.13 Experimental results for C_{BO}=30mol/m^3, N=2300 rpm, d_p=0.5mm

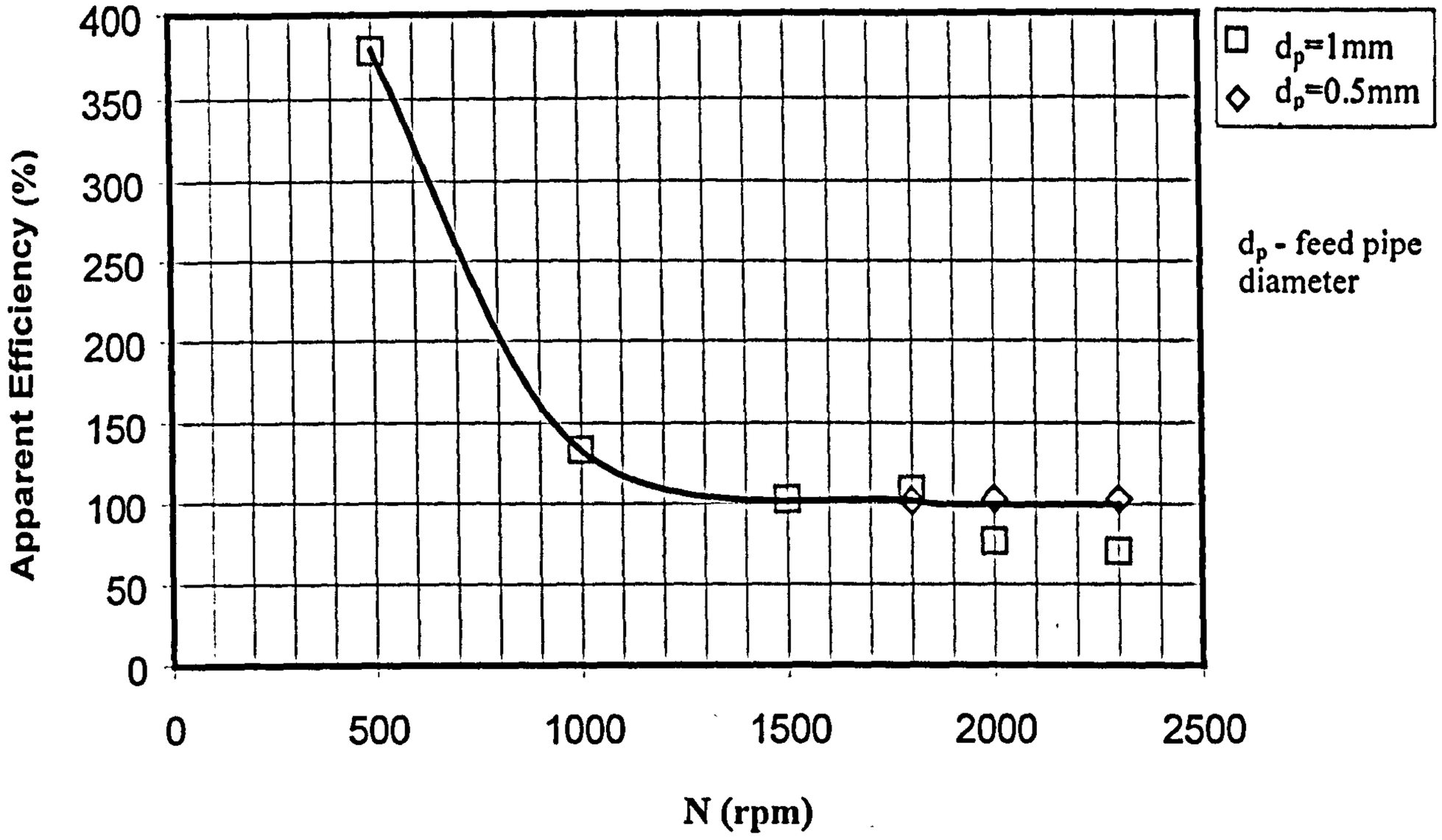


Figure 5.14 Mixing efficiency for C_{BO}=30mol/m^3

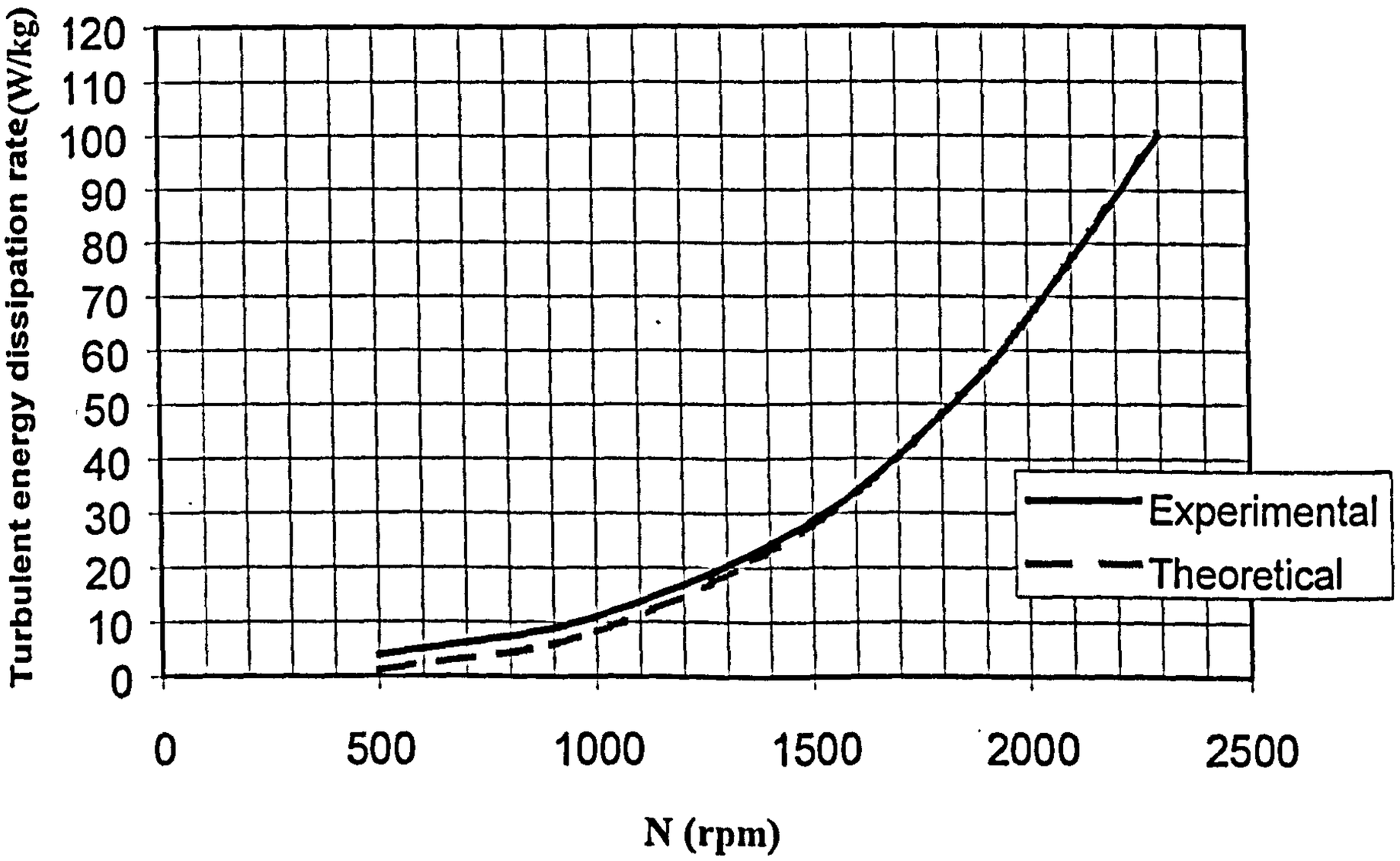


Figure 5.15 Turbulent energy dissipation rate calibration curve

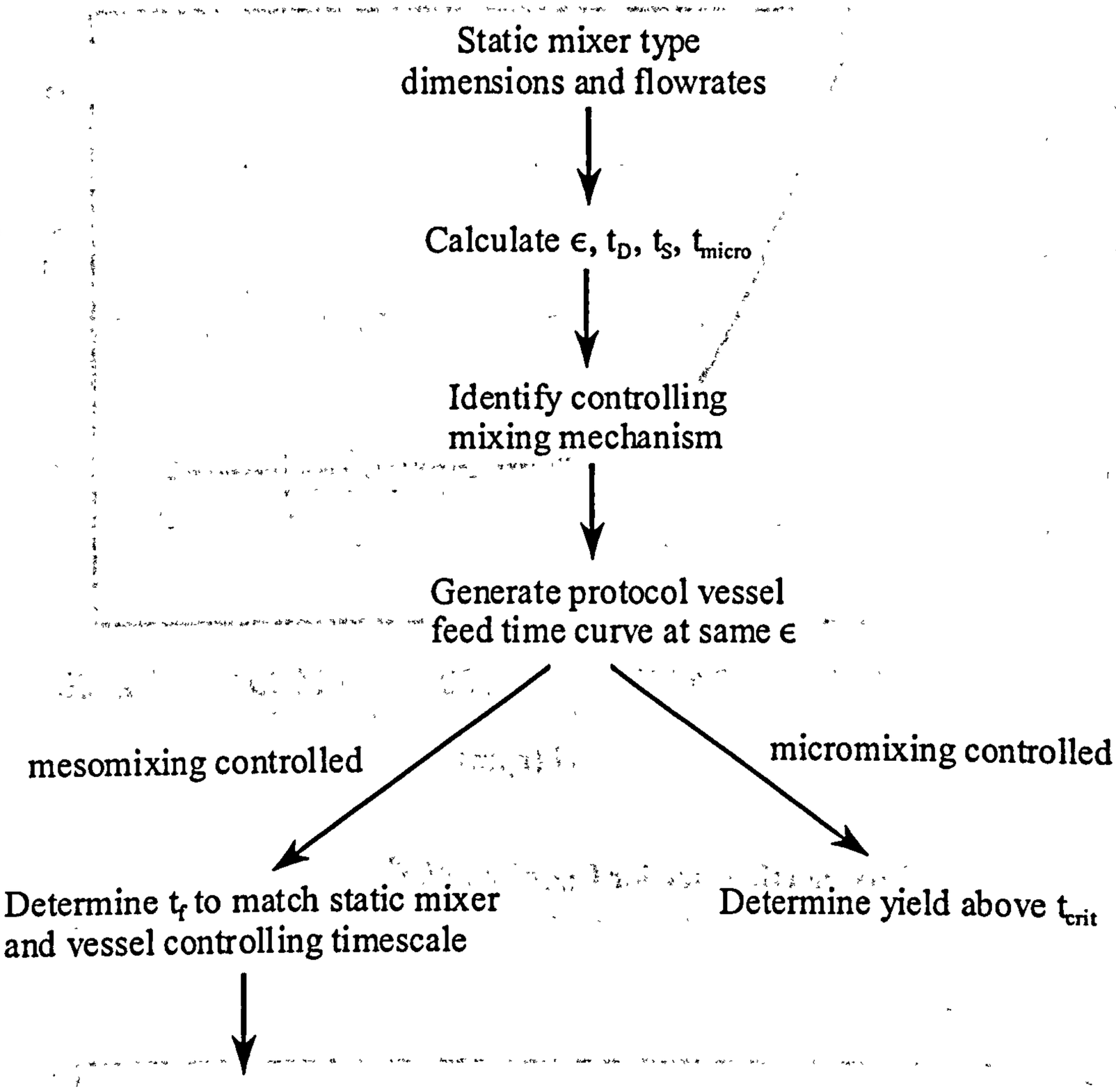


Figure 5.16 Procedures for modelling a static mixer design

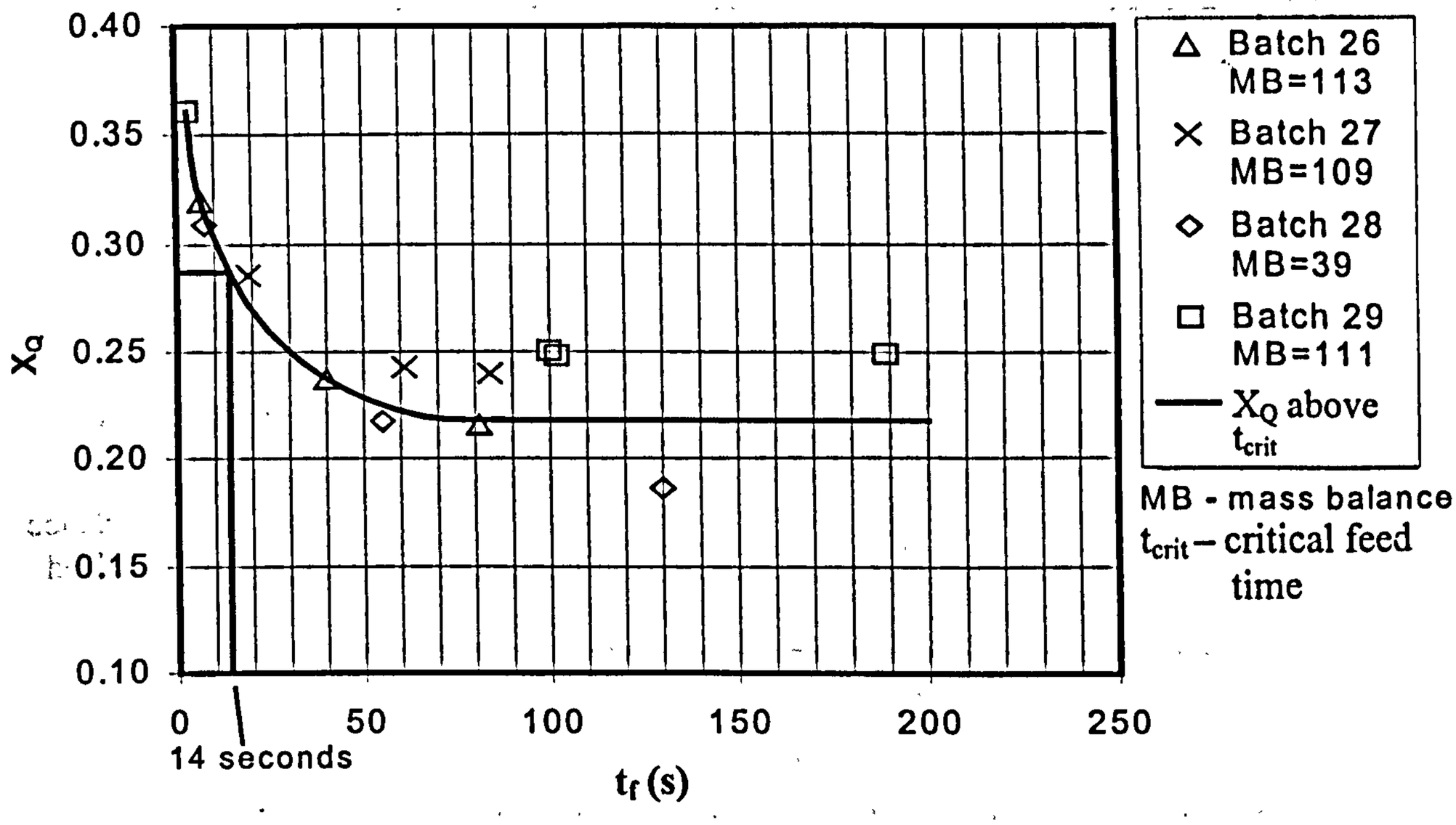


Figure 5.17 Experimental results for C_{BO}=2.5mol/m^3, 7.6 W/kg

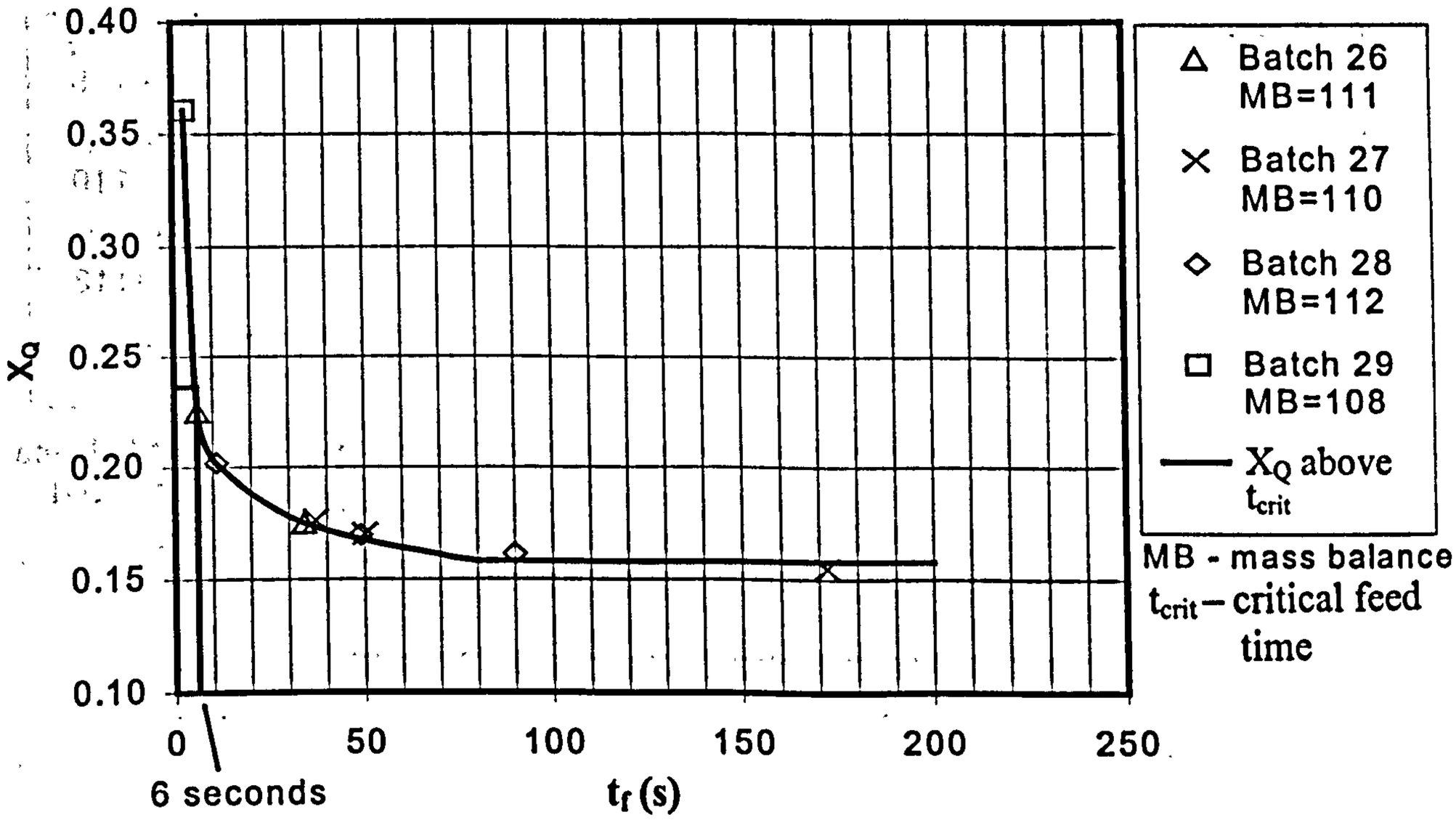


Figure 5.18 Experimental results for C_{BO}=2.5mol/m^3, 25.7 W/kg

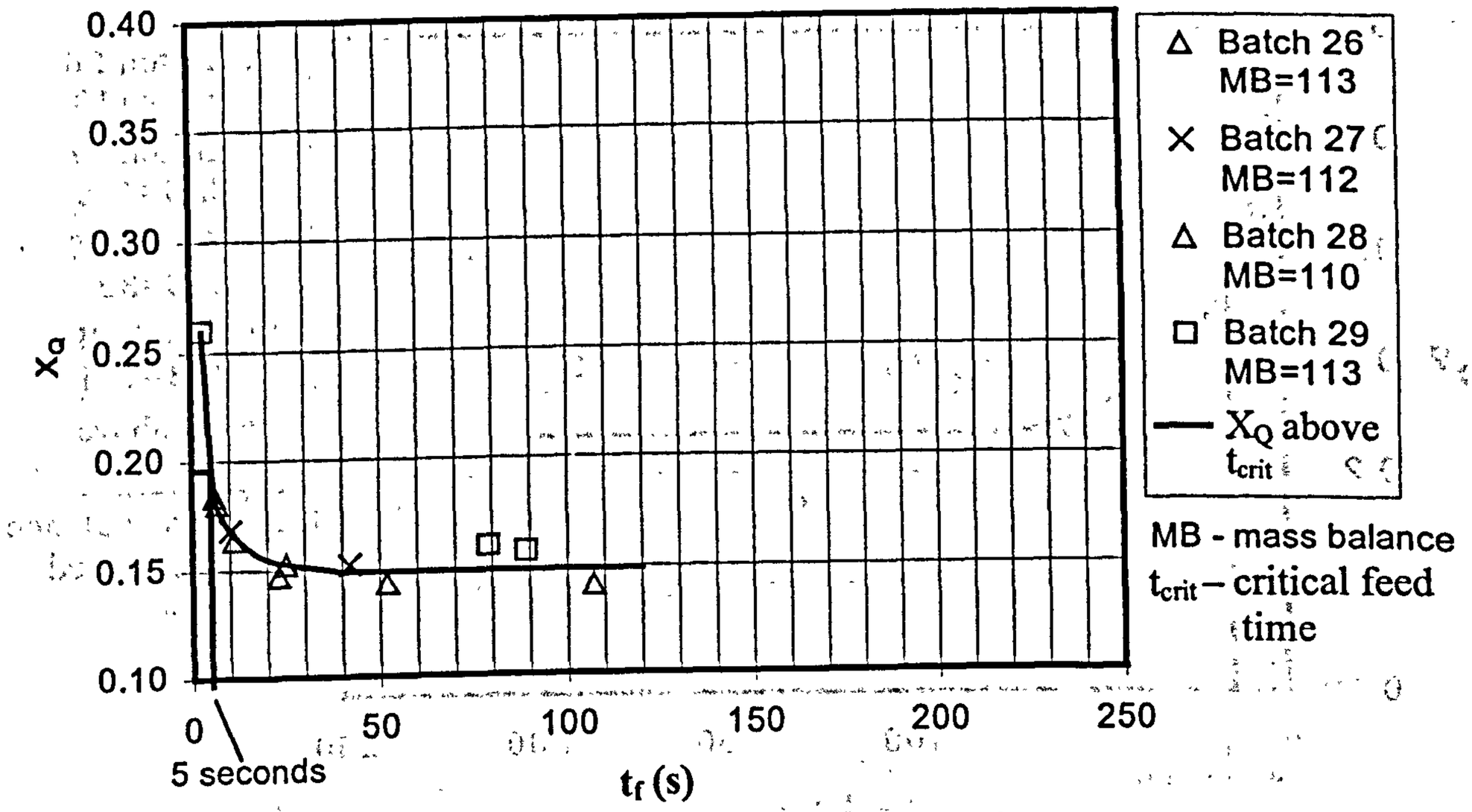


Figure 5.19 Experimental results for C_{BO}=2.5mol/m^3, 60.8 W/kg

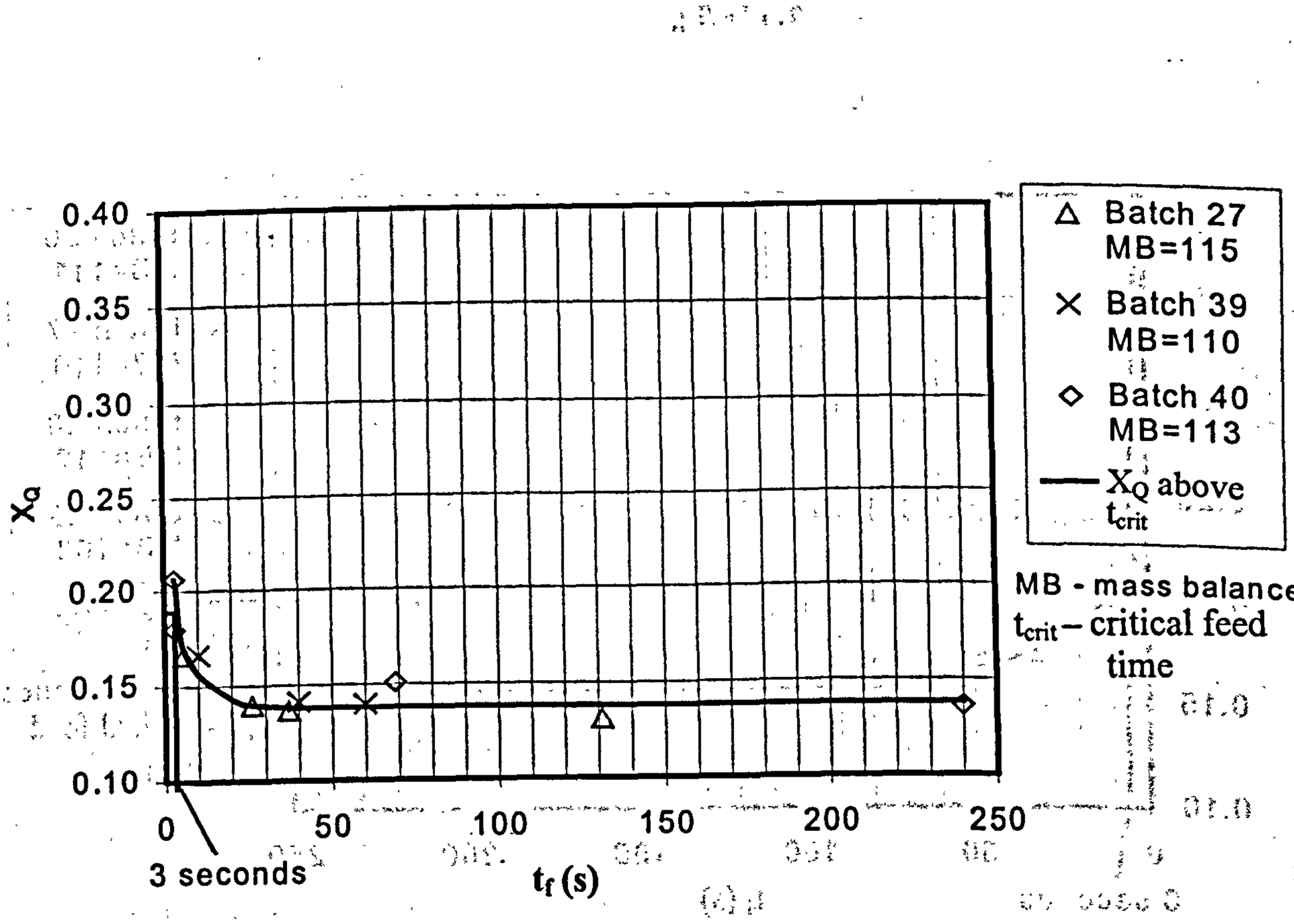


Figure 5.20 Experimental results for C_{BO}=2.5mol/m^3, 117.8 W/kg

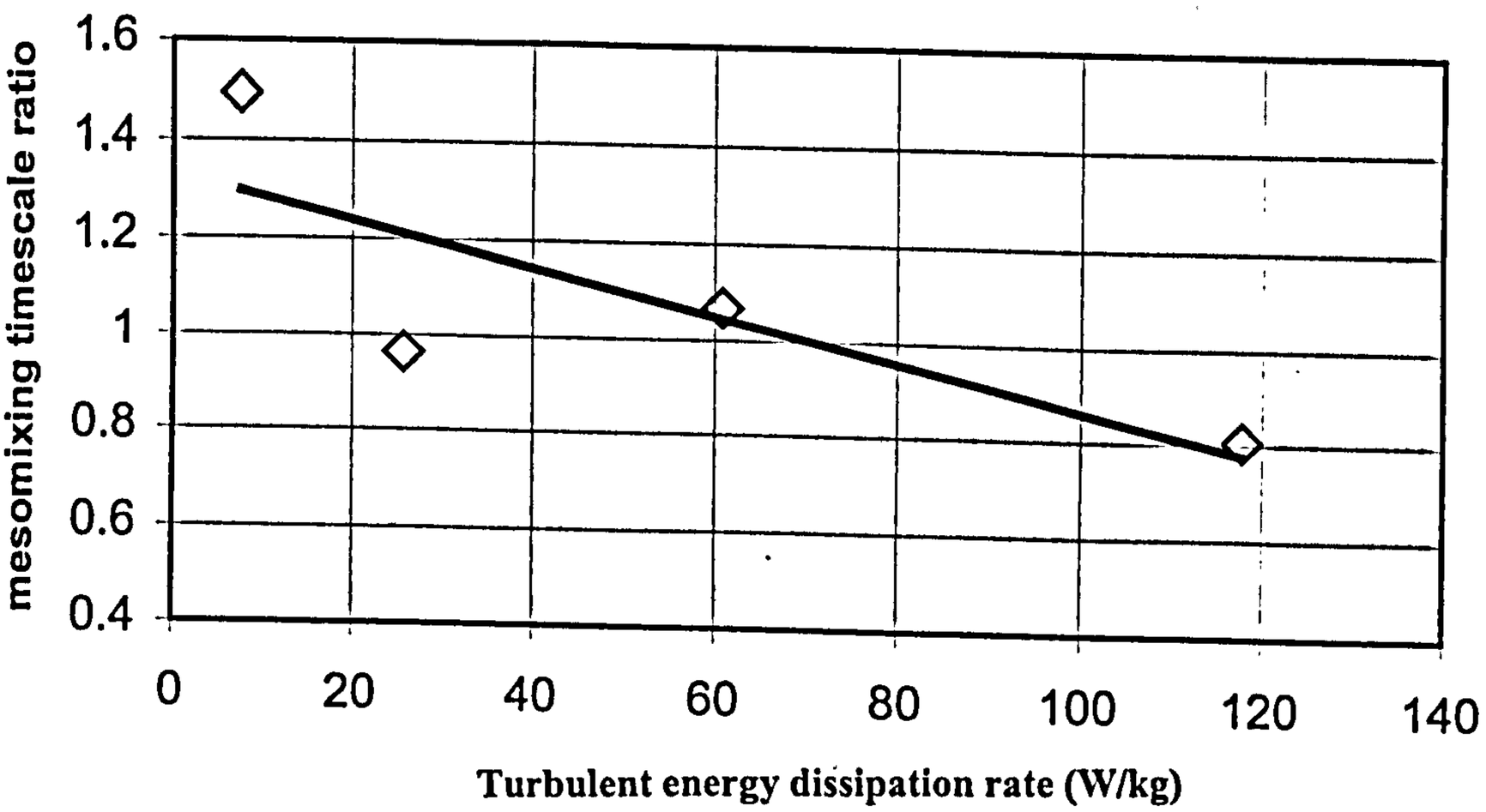


Figure 5.21 Mesomixing timescale ratio

CHAPTER 6

FULL DESCRIPTION OF THE PROCESS INTENSIFICATION METHODOLOGY

6.1 INTRODUCTION

The PI methodology is presented as a flowsheet, known as the methodology framework. This framework consists of separate procedures for each of the methodological stages and illustrates the flow of information. A full description of the methodology is given here, detailing the content of each stage and explaining why it is required. Indications of means for achieving the objectives of the stages that have yet to be developed in detail are provided. The methodology framework is shown in Figure 6.1 and applies mainly to existing chemical processes, though some of the considerations required when examining newly developed chemical synthesis routes are also given.

6.2 PARTICIPANTS

The team of workers for the methodology should be multi-disciplinary. This prevents the team focusing too strongly on one particular approach and widens the number of concepts that might be generated. The team should consist of chemists and chemical engineers, safety and plant operating personnel. For the methodology to be most effective, the participants should have some knowledge of PI, what it can achieve and how it achieves its benefits. Participants should have an open mind to the use of novel technology. Experience levels should vary as participants with little experience of the process may have fewer preconceived ideas and potentially allow other, more novel, results to be obtained.

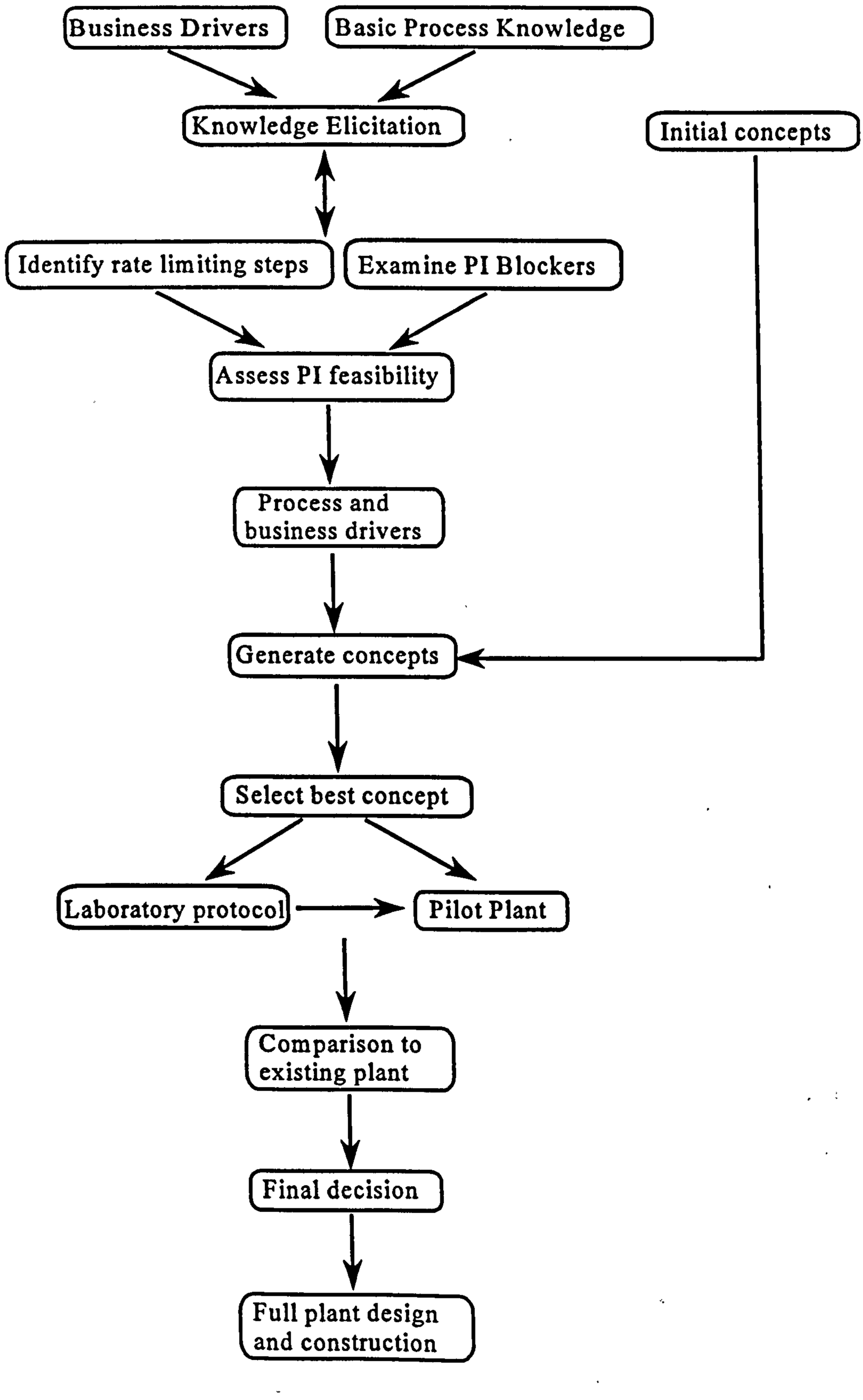


Figure 6.1 PI Methodology Framework

6.3 COMMENCEMENT

Participants should familiarise themselves with the methodological procedures to gain an appreciation of why the methodology is being followed. The PI Methodology Overview below is intended to achieve this objective.

The Initial Concepts stage, Section 6.7, should be read and the advice followed to prevent too much emphasis being placed on concepts arising in the early stages of the procedures. Reviewing the Rate Limiting Features and PI Blockers stages, Sections 6.9 and 6.10, will allow any that exist to be identified and considered as they arise.

6.4 PI METHODOLOGY OVERVIEW

Business Drivers

Determine the economic reasons for changing the process.

Basic Process Knowledge

An initial overview of the process to allow those participants unfamiliar with the process to gain an understanding of it.

Initial Concepts

Document all plant concepts that arise to allow proper consideration later in the methodological approach.

Knowledge Elicitation

Gain full understanding of the process through examination of both the chemistry and the plant it currently operates in.

Identify Rate Limiting Steps

Identify any conditions preventing the process running at a faster rate, either chemical

or mechanical. Assess how these rate limiting steps could be overcome.

Examine PI Blockers

Identify any aspects of the process that may prevent PI being applied and consider whether these blockers can be overcome.

Assess PI feasibility

Assessment of the potential for intensifying the chemical process using the results of the Knowledge Elicitation, Rate Limiting Steps and PI Blockers sections.

Process and Business Drivers

Review business drivers and add any that may arise through the PI feasibility assessment to set targets for a new plant design to meet. Process drivers are those aspects of the chemistry that the plant should be designed to meet and are identified through the feasibility assessment.

Generate Concepts

Creative problem solving session to suggest plant options for meeting the drivers.

Select Best Concept

Analyse all suggested concepts and determine the best option for the process.

Laboratory Protocol

Laboratory experiments to model the performance of the chosen plant concept and provide a basis for the design of a pilot or full scale plant.

Pilot Plant

Build and operate if required.

Comparison to Existing Plant

Use the results of the audits and protocol to compare the performance and costs of the

PI plant to those of the existing or conventional plant.

Final Decision

Decide whether the benefits of the new plant make it worth replacing the existing plant.

Full Plant Design and Construction

If a new plant is desirable, full design can then commence.

6.5 BUSINESS DRIVERS

For a project to be initiated, there must be some aspect of the current process that is not operating as efficiently as desired. This gives rise to reasons for wanting to change the plant, which are normally of an economic nature and are termed 'Business Drivers'. Business drivers are required to define the scope of the project and set financial targets for any resulting plant design to meet.

Examples of business drivers are:

- improve yield
- increase productivity
- reduce energy requirements
- improve process safety
- reduce emissions
- lower capital cost of replacement plant
- smaller plant to fit into available space
- lower operating costs

The PI questionnaire, Figure 6.2, can be used to prompt thinking of additional business drivers and provides a means of determining those which are most important. Other aspects for consideration in this stage are:

- Project objective: for example whether it is to improve the existing plant or to build

a completely new plant.

- Scope of the project: identifying the part of the process that is being examined and where the current boundaries of the project lie. It is possible that the scope may change whilst the project is in progress.
- Budget and timescale available for the project.

6.6 BASIC PROCESS KNOWLEDGE

Both the chemistry and plant are overviewed to ensure that the participants realise the process is to be examined as a whole, not the chemistry and plant in isolation. Some participants may also be unfamiliar with the process, so this will allow them to understand the basics before the detailed sections of the methodology commence. Knowledge can be gathered through the PI questionnaire, with aspects covered including:

- basic reaction scheme
- outline flowsheet
- operating conditions
- type of equipment used

6.7 INITIAL CONCEPTS

Throughout the methodological approach, ideas on how to improve the plant may arise before the Concepts Generation stage is reached. These ideas should be noted down for full consideration in proper manner. Points to note include an outline of the idea, how it occurred and what it would achieve. Initial concepts will serve to stimulate other conceptual ideas and possibly highlight other areas that need to be examined in the audit sections. Not separating out initial concepts in this manner introduces the possibility that too much focus will be placed upon these, potentially inhibiting generation of other, superior, concepts in the later stages of the methodology.

6.8 KNOWLEDGE ELICITATION

The chemistry and plant audits gather all necessary information for identifying the feasibility for intensification. Some of the information required is specific to the design of a PI plant and is not examined in standard process development procedures. In some cases there may be the potential to change the chemistry, either by the use of different reagents or catalysts, which should be examined if appropriate.

The audits take the form of checklists. These are not exhaustive and can be added to if necessary. Each aspect should be considered to ensure nothing is overlooked. It is not necessary to follow the checklists in strict order, particularly as some of the information may overlap or occur in more than one place.

6.8.1 Chemistry Audit

The chemistry audit examines the chemical synthesis route. Some parts may require experimentation to provide the information.

Below is the chemistry audit checklist and a brief discussion of each aspect.

a) Reaction scheme
b) Physical properties of process materials
c) Corrosiveness of process materials
d) Order of reactant addition
e) Minimum and maximum operating temperatures
f) Magnitude of heat release
g) Rate of heat release
h) Residence time required
i) Kinetics of reactions
j) Mechanical stability
k) Maximum possible yield and required yield

l) Byproduct formation

m) Solids formation

n) Changing the process

o) Ideal operating conditions

a) Reaction scheme

A simple reaction scheme should be drawn out for easy referral. Include catalysts, solvents and chemical equilibrium.

- Determine why these particular reactants/solvents/catalysts are used. For example, is solvent used in excess to boil off and remove heat of reaction?
- What byproducts are formed?
- Why is this particular stoichiometry used? E.g. is it to promote the desired reaction or to minimise waste?

b) Physical properties of process materials

Determine the viscosity, specific heat capacity, density, phase, melting and boiling points of each component or component mixture in the system. Variation of properties with shear, temperature or time should also be noted. Does any phase change occur during the process?

c) Corrosiveness of process materials

Corrosiveness will determine the materials of construction required on the plant. This could be an important consideration as some items of equipment may not be available in particular materials of construction. See also Section (c) of the plant audit.

d) Order of reactant addition

The order of addition will have practical implications on the design of a plant as it is necessary to know which is the bulk flow and which is the additive stream for continuous processing.

- In what order are reactants added during laboratory testing?
- Is this the same as at full scale operation? If not, why not?

- Are they charged to the vessel as batch, semi-batch or continuous? (See Section (g) of the plant audit).
- Why is it done this way? E.g. to control exotherms or maximise yield.
- Have other orders of addition been tried previously and what was the result?
- What would the consequences be of adding in a different order, either beneficial or otherwise?

e) Minimum and maximum operating temperatures

Some processes have a maximum safe operating temperature, above which problems such as thermal degradation of products or potential runaway conditions could occur. This temperature value should be identified and avoided.

f) Magnitude of heat release

Find the adiabatic temperature rise which will show whether there is the potential for the reaction to reach runaway temperatures or undesirable conditions. Calorimetry is the normal procedure for examining thermodynamics. Simple laboratory experiments can be run for less extreme reactions by adding reactants and measuring the temperature rise. If this is done, ensure that no heat is lost through the sides of the vessel as this can mask exotherms that may prove significant on the larger scale. Include endotherms in this analysis.

g) Rate of heat release

How quickly does any heat release occur? Observing the rate of temperature change after reactant addition under well-mixed conditions is the simplest means of achieving this. Rate of heat release can give some indication of the reaction kinetics.

h) Residence time required

How long does the reaction take to go to completion in a small vessel where there are no restrictions on heat transfer or mixing? Reactants should be added in stoichiometric amounts as rapidly as possible. This will provide a basis for comparison with the actual residence time experienced on the existing plant, determined in Section (i) of the plant

audit, and also provide a residence time for the new plant design to meet. Knowing the residence time may also contribute towards determination of the kinetics as slower reactions require longer residence times.

i) Kinetics of reaction

Gather any knowledge on the kinetics of the reaction scheme. Comparison to similar reactions may give some indication of kinetics if these are otherwise not known. It is not necessary to know the exact kinetics, but should be sufficient to say, for example, the reaction is complete after twenty seconds. Steps g) and h) may contribute towards the inference of the kinetics. Check how sensitive the kinetics are to temperature, as an increase in temperature can significantly increase the reaction rate.

It is possible to do mixing-sensitivity experiments if the reaction is part of a competitive reaction scheme, using the laboratory protocol vessel described in Section 5.5. If the reaction is slow, the reactants will be fully blended before reaction occurs, so varying mixer speed will have no effect on product yield. Faster reactions will tend to occur in a small reaction zone near the feed pipe, so product yield would be expected to vary depending upon the mixer speed. Any improvements in product quality at higher levels of mixing will indicate the benefits of intensified operation.

j) Mechanical stability

Some fluids, for example emulsions, may lack the strength to be subject to the extreme mechanical conditions provided by PI equipment without degrading. The process fluids should be tested for mechanical strength by subjecting them to a varying range of mixing energy input using a vessel such as the laboratory protocol vessel described in Section 5.5. If the product does break down, the mixing conditions that cause this can be determined, providing a constraint upon the conditions that any subsequent plant design can provide.

k) Maximum possible yield and required yield

Determine the best possible product yield or selectivity. For example, for competitive

reaction schemes where the desired reaction is the fastest, run an experiment in the laboratory protocol equipment with feed above the critical feed time and high turbulent energy dissipation rate. The yield value will then set a benchmark for all other laboratory, pilot and full scale equipment to achieve. Is it actually desirable to achieve this yield? For some products a lower yield or product quality may be acceptable, so the process should not be over-designed.

l) Byproduct formation

If byproducts are formed, what is it that influences the formation? Causes could include:

- temperature of operation
- contact of product with fresh reactants
- degradation over long residence time
- contact of different products over long residence time

What conditions would be required in an ideal reactor to avoid any of the above occurring?

m) Solids formation

Solids can be a major problem for PI application, as the small PI equipment channels can easily block. Apply the following checklist if solids exist in the process:

- Are the solids: products; byproducts; feed materials; intermediates; catalysts?
- Are solids desirable? E.g. for pharmaceuticals where it can ease purification.
- Can solid byproducts be avoided? (see checklist in (l) above).
- Could solid feedstock be fed either fed as a slurry, melted or dissolved?
- Could solid catalysts be suspended on a wire mesh across the flow or coated on some other surface?
- Do the solids only form under certain conditions?
- How large are the solids particles? - small may be acceptable for PI.
- Is the solid size critical? E.g. crystallisation.
- If solids are formed during the process, how quickly do they form?
- Could intensive mixing prevent unnecessary agglomeration or crystallization?

- Do solids remain free or stick to surfaces which can cause fouling?

The above checklist is not exhaustive, but should prompt thinking on the form of the solids present in the system and whether these may cause a problem for intensified processing.

n) Changing the process

It may be possible to change the synthesis route in some way to achieve faster kinetics or higher yield. The Britest project (see Section 3.5) is developing means of achieving this objective. Points to consider are:

- increasing concentrations will increase the reaction rate
- use of a catalyst
- use of different reagents in any stage of the make-up
- phase of operation - it may be possible to operate more efficiently in a different phase, for example gas instead of liquid

o) Ideal operating conditions

Variables that can be examined include temperature, pressure, pH, mixing conditions. Increasing temperature will increase the rate of most reactions, possibly increasing reaction rate enough to prove viable for PI when otherwise it would not have been. For viscous fluids, increasing temperature can decrease viscosities and make them easier to handle. Increased pressure will allow higher temperature operation for liquids that may otherwise boil off. Results of the mixing-sensitivity experiments in step (i) can be used to determine the required mixing environment. If no product quality improvement is noted above a certain mixer speed, this will allow determination of the maximum required turbulent energy dissipation rate.

6.8.2 New Process Development Considerations

If the methodology is being applied to the development and selection of a new synthesis route, a basic chemistry audit is required to allow a preliminary assessment of the

feasibility for intensification. The following stages of the main chemistry audit are required during the initial assessment. Other factors have no immediate bearing upon the new process feasibility study, but a full chemistry audit will be done on the chosen synthesis route and the PI methodology followed from there on.

a) Reaction Scheme

b) Physical Properties - only need viscosity and phase of each component or mixture

i) Kinetics of reaction - detailed kinetics are not essential, just an appreciation of how long the reaction takes to go to completion if it is not mechanically limited.

l) Byproduct formation - if byproducts are formed, what is it that influences the formation?

m) Solids formation - apply the solids checklist if solids exist in the process.

n) Changing the process - the opportunity for changing the process is highest here.

Ideally, synthesis routes with a high potential for intensification will be selected. These will be the routes with the fewest PI blockers, listed in Table 6.1. Reactions with fast kinetics and liquid-phase operation are indications of high PI feasibility. The role of the PI feasibility assessment of new synthesis routes is given in Section 4.12, with the primary motive being to ensure that reactions which may be suitable for intensification are not screened out on the basis of being difficult to handle or control under conventional operation. PI operation may allow what are perceived as hazardous reactions to be operated safely within smaller, intensified equipment. The final choice of synthesis route will depend upon a number of economic and operational factors, as mentioned in Section 2.6.1.

6.8.3 Plant Audit

Most of the plant audit assesses the performance of the existing plant. This aids in the understanding of the process as a whole and shows particular problems that should be targeted in the design of the new plant. Information gathered may also prove beneficial or essential for the design of a new plant. The last stages of the plant audit define what

an ideal plant would produce, setting targets for the new plant design to achieve.

a) Physical dimensions of equipment
b) Process flowsheet, mass balance and heat balance
c) Materials of construction
d) Operating conditions
e) Mixing capability
f) Heat transfer and utilities
g) Feed addition
h) Rate of feed addition
i) Length of batch times
j) Upstream and downstream processing capacity
k) Obvious problems with the plant
l) Current production output and rate

For the desired plant:

m) Desired production output and rate
n) Desired flexibility of the plant

a) Physical dimensions of equipment

Obtain the dimensions of the major plant items, including heat transfer equipment. This knowledge will aid the understanding of the plant and will be required should calculations on the performance of the plant be needed. A direct size comparison to any PI plant concept will also be possible.

b) Process flowsheet, mass balance and heat balance

A basic process flowsheet will allow visualisation of the existing plant. The mass balance is required to aid understanding of the process and will form the basis for the new plant design. The heat balance will show the duty required of the new plant.

c) Materials of construction

This ties in with the evaluation of process material corrosiveness, Section (c) of the chemistry audit. Glass-lined vessels are frequently used in the chemicals industry as they are chemically resistant, but if glass is used, ensure that this is not just because it is standard. In some circumstances, the material of construction can affect the reaction that occurs.

d) Operating conditions

- Temperature, pressure, pH.
- Are these profiled over time?
- How tightly are these controlled?
- Why are these conditions or profiles used? E.g. are they just within a standard operating range, or is it a requirement of the chemistry?
- What would the consequences be of operating under other conditions?
- Is there a history of problems encountered under other operating conditions?

e) Mixing capability

Determine the means of mixing within a vessel. Find the size and type of any impeller and rate of rotation. It is then possible to calculate mixing timescales and turbulent energy dissipation rate within the vessel should this be required in any other stage of the project.

f) Heat transfer and utilities

- How much heat is the equipment capable of removing? This will assist in identifying the rate limiting steps as heat transfer from vessels is a prime cause of long processing times.
- What utilities are available on-site and what temperatures are these at? This could inflict constraints upon the operating conditions of a new reactor.
- Does temperature of utility vary with ambient conditions? What are the ambient conditions?
- What flow rates of utilities are available?

- Is utility supply constant or will it fluctuate with demand on the rest of the site?

g) Feed addition

The considerations below relate to those in the chemistry audit Section (d).

- Is the mode of operation batchwise, semi-batchwise or continuous?
- Where is feed added (surface, dip-pipe, impeller region?). Feeding to the impeller region results in more rapid blending of the feed stream.
- Is any pre-mixing of reactants done upstream or even in same vessel before the rest of the reactants are added?
- Order of feed addition. Is this the same as in the laboratory?

h) Rate of feed addition

- If semi-batch feed is used, is it fed quickly, or at a slower, more controlled rate?
- Is it fed slowly due to heat transfer limitations and/or to control byproduct yield? Slow feed could be a result of poor mixing or heat transfer.

i) Length of batch times

Applies mainly to operation in STRs.

- How much of the batch time is for reaction and how long is required for other duties, for example heating or cooling between reaction stages?
- How does the reaction residence time compare with that in small scale laboratory experiments (determined in Section (h) of the chemistry audit)?
- If the batch time is increased on scale-up, why does this happen? This could indicate that the reaction environment is not ideal for the process.
- Are products left standing for a long time for 'scavenging', i.e. reacting the last few percent? This could increase byproduct formation.

j) Upstream and downstream processing capacity

Limitations in feedstock or downstream processing and storage may restrict the production rate and schedule of the new plant. Determine the quantity and feed rate of raw materials available and the downstream processing abilities.

k) Obvious problems with the plant

Are there any aspects of the current plant which are obviously causing operational problems? Fouling is one possible option. Any previous operating difficulties or incidents should be examined to try and show why they occurred and how they could have been prevented. This will show any pitfalls that a new plant should avoid.

l) Current production output and rate

The current output rate is the amount produced in a given timescale, for example amount per day or per week when the plant is operational. Some plants may only operate for a short period per week. The production rate may be limited by other factors up and downstream.

- What is the total production output over the whole year?
- For batch operation, how many batches per year is this?

m) Desired production output and rate

A new plant will be designed for the required output per annum, potentially with additional capability should increased output ever prove necessary. Consider whether the production will be fully continuous, or made in campaigns for, say, one week per month. This will set the production rate required of the plant. An estimated rate can be used as a basis for the design and mass balance calculations. The final value may depend on other factors which come to light as the project progresses.

n) Desired flexibility of plant

Is this going to be a dedicated plant or multi-product? If multi-product, what other reaction schemes are being considered? How similar are the other reaction schemes to this one? A requirement for flexibility may impose restrictions upon the design of the plant. PI plant is designed to meet the needs of the particular process, but it is possible to increase the flexibility of a PI plant by having inter-changeable processing units within a standard layout of pipes and utilities supply.

6.9 IDENTIFY RATE LIMITING STEPS

From the results of both the plant and chemistry audits, any rate limiting steps can be identified. Rate limiting features can be either mechanical or chemical. Participants should determine why the rate limiting features occur and consider means by which these can be overcome.

Mechanical limiting steps are features of the plant equipment that prevent the reaction from running at a faster rate. Limited heat transfer from the vessel and poor mixing which combine to produce long feed addition times are two examples. Ideal operating conditions determined in the Chemistry Audit Section (o) could be compared to the conditions the plant actually produces to determine where the current plant fails to match the requirements. Reactant availability from an upstream process, or the downstream processing capabilities, may also prevent a higher production rate.

Chemical rate limiting features are to do with the nature of the chemicals, where nothing that is done mechanically can increase the reaction rate. Slow reactions are an obvious example. Absorption into solids and denaturing of catalysts over the process lifespan are other chemical rate limiting features.

6.10 EXAMINE PI BLOCKERS

Blockers are those properties or conditions of a process that may prevent the use of PI. The audits should identify what these blockers are and encourage discussion on means of overcoming them. Some potential blockers and points of consideration are shown in the Table 6.1 below. Most are 'process' blockers to do with the nature of the chemicals themselves. Others are 'business' blockers which are practical problems encountered when designing or operating PI plants. Blockers may include some of the rate limiting steps.

Table 6.1 Examples of PI Blockers

Blocker	Points to consider
Solids	Why are solids present? See chemistry audit Section (m) for more points
Slow reaction	Why is it slow? Can the rate be increased?
Equilibrium	Is there a reversible reaction that may limit the maximum conversion? This can possibly be overcome by removing products as they are formed.
High viscosity	High viscosity impedes mixing. Can viscosity be reduced?
High viscosity liquid / gas mixture	Can this situation be prevented? Can liquid viscosity be reduced?
High viscosity ratio	This may impede mixing. Can viscosities be made more equal?
Fouling	Some process fluids are prone to fouling, which may cause problems in the narrow channels of PI equipment
Boiling reactor conditions	Is a solvent boiled off as heat removal duty? If so, can heat transfer duty be increased to remove the need for this?
Multi-product plant required	Are products very different, or similar? If similar, PI equipment could be flexible enough to operate them all.
Materials of construction	PI plant might not be available in the materials of construction needed to resist some corrosive conditions
Utilities	Availability of on-site utilities can restrict the choice of process.

6.11 ASSESS PI FEASIBILITY

The potential for intensifying a process is determined by pulling together the results of the audits, blockers and rate limiting steps into a mid-methodology report. Any blockers that cannot be overcome may restrict or eliminate the potential for intensification. If the process is only mechanically limited and has no blockers, this will indicate a high PI feasibility. Any significant chemical rate limiting features may

result in low PI feasibility. Intensification characteristics of chemical reactions include:

- fast kinetics
- non-solid phase
- high heat release
- mixing-sensitivity

If it is determined that the process cannot be intensified, the information gathered above can still be used to identify means of improving the existing plant or operating procedures. This can be achieved by following the rest of the PI methodology which applies equally to the design of new plant or the redesign of an existing plant.

6.12 BUSINESS AND PROCESS DRIVERS

The methodology has now completed the feasibility assessment and moves into the design stage. The first task is to define the problem that is being approached by determining the drivers. Process drivers are those characteristics of the chemical reaction scheme that determine the operating conditions in, and required performance of, reactor equipment to allow the process to run at its most efficient rate. Business drivers are the economical reasons it is desirable to change the plant.

The problem definition at the start of the methodology consisted of only the business drivers. However, the real problem to be solved is defined by the process drivers which, when met, will then allow the business drivers to be achieved. For example, instead of the problem being the original business driver of 'Improve productivity', the audit may reveal that the process is heat transfer limited, so the problem is now 'How do I improve heat transfer so I can improve productivity?'. Examples of process drivers are:

- process kinetics which dictate the rate of mixing required
- quantity and rate of heat released
- residence time required

- turbulent energy dissipation rate that gives the desired process performance

The business drivers should be reviewed to highlight the targets to be met by the plant design. Knowledge gained during the audits may strengthen some business drivers and create others. It is likely that some of the drivers are more important than others, so these could be ranked to prioritise the aspects the plant design should meet.

6.13 GENERATE CONCEPTS

A creative problem solving session is held to suggest concepts for meeting the drivers and hence intensifying the plant. Any initial concepts arising during the project will provide a starting point for discussions. Literature or patent searches could be carried out beforehand to find how specific problems have been approached in the past. The problem could be broken down into individual drivers to be considered separately, but it is still important to consider the process as a whole.

It is desirable to avoid going into the 'equipment driven' mode where the only suggestions are those relating to existing and standard pieces of equipment. Under these circumstances, the obvious way to improve the process may be missed. Flowcharts could be used to summarise the decision routes leading to selection of certain types of equipment, such as Figure 3.2 for selecting between static mixers and conventional stirred vessels. Once a number of options have been generated, these should be examined to consider how they could be improved.

6.14 SELECT BEST CONCEPT

All of the concepts should be analysed and discussed to see how well each of them matches the drivers and then choose the best overall concept. Improvements to the concepts or completely new concepts could still arise here. The concept generation can

be returned to if none of the concepts offer a practicable or fully beneficial solution. In addition to the drivers, the following considerations should also be made:

- laboratory experiments required to prove a concept
- capital and operating costs
- potential savings and benefits
- confidence in the design
- risk
- timescale to construction
- complexity

6.15 LABORATORY PROTOCOL

It is desirable to run experiments to model the performance of the chosen plant concept and quantify the benefits that can be achieved. This can also be used to aid in the selection of the best overall concept if the decision is not clear-cut in the above stage. The protocol experiments will provide a basis for design of the pilot or full-scale plant.

The equipment and procedures for laboratory protocol experiments to model performance of static mixers are discussed in Chapter 5. These procedures still require further development.

6.16 PILOT PLANT

Build and operate a pilot plant if required. The laboratory protocol can assist in the design of the pilot plant by identifying the operating conditions it should provide. The effects of scale upon the process have to be taken into account when operating a pilot plant to ensure that the conditions it operates under are the same as will be achieved on the full scale plant.

6.17 COMPARE WITH CONVENTIONAL PLANT

Compare the performance of a conceptual plant to the existing conventional plant. The performance is quantified through the protocol and/or pilot plant operation. The conceptual plant should be rated on how it achieves the drivers and how, if at all, it has improved upon the existing plant. Examples for comparison include capital and operating costs, energy efficiency, safety and process performance. List the strong and weak points of both the existing and conceptual plant. Showing that the conventional plant is not fully suitable for a process due to mechanical rate limiting features could be just as important as showing the benefits achievable by a PI design.

6.18 FINAL DECISION

A final decision is made on whether to proceed with the full design of the plant. This will involve assessing whether the achievable benefits justify the risks and costs associated with development. A high risk factor and long lead time to commissioning may rule out the use of PI, even if significant financial and operability benefits exist.

6.19 FULL PLANT DESIGN

Once the plant concept has been determined, the full mechanical design and construction is carried out. These operations are outside the scope of this methodology.

6.20 FEEDBACK

An additional stage after the methodology is completed is to review the project. This should determine the strong and weak points of the procedures undertaken, disseminate any new knowledge and update the methodology contents as necessary.

Process Intensification Questionnaire

PART A: BUSINESS ASPECTS

Why would a new/improved plant be required? Tick next to required answer.

[ ] Safety
[ ] Improved efficiency
[ ] New products
[ ] Upgrade existing capacity
[ ] Replace existing capacity
[ ] Expand capacity
[ ] Other (please specify)

What benefits would be sought? Please rate from 1 (= unimportant) to 4 (= critical factor)
Rating below:

[ ] Improved product quality
[ ] Low byproduct formation
[ ] High conversion
[ ] High product yield
[ ] Time to market
[ ] Inherently safe operation
[ ] Small plant (reduce footprint/skyline)
[ ] Low capital cost
[ ] Low energy usage
[ ] Other (please specify)

Would the new/improved plant be dedicated to one particular process or be multi-product? If multi-product, how similar are the other products to the one in question?

What production capacity would be required (tpa)?

What production campaign would you follow? i.e. operation continuously or in campaigns?

PART B: TECHNICAL ASPECTS OF THE PROCESS

1. Brief Summary of Process

Describe **briefly** the raw materials, process steps involved, products and byproducts.

2. Raw Materials

Define state of raw materials, physical properties and form (eg solid with particle size x, liquid with viscosity y).

3. Preprocessing

What preprocessing steps are used (eg dissolution)? How much feedstock is available and how frequently?

4. Downstream Operations

What downstream separations or processses are required? Do these operate continuously or batchwise? What is their capacity?

5. Flowsheet

Please sketch an outline flowsheet of the existing process if possible.

6. Reaction Stage(s)

What is the chemistry of the process? Include:

- reaction steps (including any known side reactions/byproduct formation)
- kinetics of each step (order of magnitude estimates of rate constants, instantaneous, slow)
- exothermicity

(where details are not available, please give any related evidence)

What are the reaction conditions?

- phases of reactants/solvents
- fluid viscosities
- normal reaction conditions (temperature, pressure, concentrations)
- form of product and significant byproducts (e.g. in solution; precipitate; liquid etc)

Figure 6.2 Process Intensification Questionnaire

CHAPTER 7

DISCUSSION AND CONCLUSIONS

7.1 INTRODUCTION

The need for a PI methodology has been identified through the literature survey in Chapter 2. This shows that although PI can provide significant benefits to the chemicals industry, application is not widespread. A major cause of this limited application is the lack of proper design procedures to show how the design of PI plant should be approached. Chapter 3 demonstrates this lack of PI consideration in published process development and safety methodologies.

The resulting PI methodology developed to overcome the lack of PI procedures is based around a flowsheet, known as the framework. Development of the framework commenced by setting out the ideal procedures to meet the PI definition of designing the plant to meet the needs of a process. The PI methodology identifies the needs of the process, defined through the process and business drivers, in turn determining the feasibility for intensification. This information is then used to design a suitable plant. These initial, ideal, procedures were expanded through contact with industrialists and the aid of industrial case studies into the final methodology framework. The flowsheet approach was maintained as it provides a simple and easily referenced tool that guides the user through the required considerations in the correct order.

The PI methodology is discussed below, describing the approach taken and highlighting the areas where there is still the scope for further development. This includes consideration of the laboratory protocol, which is an integral part of the overall methodological approach, showing how a redesigned protocol vessel and procedures would widen the potential applications.

7.2 APPLICATIONS

It has been determined in Section 4.2 that the PI methodology will be of most use when applied to the redesign of existing processes, rather than examining the whole of process development from selection of the chemical synthesis route onwards. A major reason for this decision is that timescales of plant redesign can allow more flexibility for examining new plant options as there is less of a need to get a product onto the market. Work is also being carried out by other researchers on the redesign of chemical synthesis route selection procedures, within which PI will only be one of a number of considerations. Therefore, any work done in this area would largely be duplicating what is already being done. Despite the decision to focus on existing processes, the need to introduce PI into the design process at the earliest opportunity is recognised. Consequently, the PI methodology includes a section highlighting areas where the existing procedures for development of new processes should be changed to ensure the concept of PI is not overlooked where it can achieve the greatest benefits.

It has been decided to focus the PI methodology upon intensification of chemical reactors, as improving the performance of the reactor will benefit the entire process. As a result, the Knowledge Elicitation section of the methodology has been developed mainly to assess chemical reactions and reactors. The overall approach of the methodology and many of the points considered during the audits and PI feasibility assessments can be applied to the intensification of unit operations other than the reactor as these still relate to designing the plant to meet the needs of the process.

7.3 LAYOUT AND APPROACH

Each section of the framework is a separate set of procedures for achieving a particular objective. Chapter 6 contains a brief outline description of the PI Methodology to explain why each section is needed. The participants can then look up the more detailed aspects of the section as required. This has the effect of layering the detail of the

methodology, simplifying its usability.

The straight-through format of the framework does make it difficult to represent some of the repeated sections/iterations that may occur. This is particularly true for the Examine PI Blockers and Identify Rate Limiting Features stages. These stages are placed in the methodology to formally summarise the findings from the audits, but these stages should be reviewed at the commencement of every project and kept in mind throughout the audits. This will allow those blockers and rate limiting features that may be present to be identified and potential means of overcoming them considered and explored without subsequently having to return to the audits. The methodology represents this as a double-headed arrow, with the introduction to the methodology stating how this aspect should be approached.

A number of checklists are included in the methodology, particularly in the Knowledge Elicitation and Examine PI Blockers stages, that set out the required information and means of achieving it. These checklists have been compiled over the duration of the research from literature, industrial contact and case studies. A PI questionnaire included to assist in the identification of business drivers and gathering of basic process knowledge (Figure 6.2) also acts as a checklist. Any additional considerations arising from projects can be added to the checklists as necessary for future use.

7.4 INITIAL CONCEPTS

Strictly following the PI definition of designing a plant to meet the needs of the process, generation of concepts for the plant should be left until all the knowledge has been gathered and the drivers determined. However, it was shown by Case Study 1 in Section 4.6 that participants have a tendency to quickly focus on one particular solution to a problem, rather than waiting until the appropriate stage. Accepting ideas too early can introduce bias into the rest of the methodology and potentially suppress superior concepts. To avoid this scenario, the Initial Concepts stage was introduced to

encourage participants to make notes on concepts as they arise for proper consideration at the appropriate stage and therefore allow generation of the best possible plant design.

7.5 LABORATORY PROTOCOL

A laboratory protocol has been developed to allow experimental modelling of PI, which has been shown to be unachievable using current laboratory techniques. This will serve to increase confidence in the operation of PI by demonstrating the performance that can be achieved in relatively simple equipment. Without the protocol, the PI methodology would be only a theoretical tool that does not provide demonstrations of the concepts that it generates. The main aspects of the protocol is discussed in Section 7.7.

7.5.1 PI Feasibility

The chemistry audit requires an investigation into mixing effects on the chemical reaction scheme and knowledge of reaction kinetics to assist in the determination of PI feasibility. Examination of mixing characteristics is currently not included in process development experimentation, whilst kinetics are rarely known. Some simple mixing experiments are suggested that in turn can be used to infer reaction kinetics. The guidelines already given in the methodology should prompt participants to consider the true speed of the reaction kinetics, though further work is required to develop fuller procedures for the determination of mixing effects and chemical kinetics.

7.5.2 Comparison to Static Mixer Performance

Demonstration of the performance of particular PI plant concepts will aid the design of full scale or pilot plants. Benefits of this approach are the simplicity of the equipment and experiments, low cost and low consumption of chemicals compared to a continuous reactor. Findings from this work show that it is possible to achieve the same performance in a stirred vessel as a static mixer, though a much wider experimental

programme is required to develop this approach further, as detailed in Section 5.8.

7.6 INTEGRATION OF ASPECTS FROM OTHER METHODOLOGIES

Wherever possible, means of achieving each methodological stage have been included within the methodology procedures. It has been identified that established tools and techniques could be incorporated into the PI methodology to provide procedures for stages which are yet to be fully developed. These are described below.

7.6.1 'Why-Why' Approach

Identifying causes of problems or potential for intensification could be achieved through the 'why-why' approach (Section 3.2) where the participant is consistently prompted to consider reasons why a particular phenomena occurs. This approach would be beneficial for determining the rate limiting features as these will be at the root of many of the problems experienced on the plant. Information for this analysis would be provided through the chemistry and plant audits.

7.6.2 Numerical Ratings

Ratings are a means of quantifying points of comparison and aiding in the identification of the best options. This approach is employed in many of the methodologies reviewed in Chapter 3. Areas of the PI methodology that may benefit from a ratings approach includes the assessment of PI feasibility, which depends upon any identified PI blockers and rate limiting features. If the blockers and rate limiting features can be overcome, the PI feasibility is high. If not, PI feasibility is low. A numerical rating approach would give, say, the kinetics a score on their relative speed, with a high score being fast kinetics and a low score slow kinetics. Other factors could be rated in this manner and combined, with a high overall score indicating high PI feasibility. Selection of the best plant concept could also be achieved through a ratings approach.

The large number of factors needed for comparisons within the PI methodology would require a significant amount of time for ratings to be developed. Even then, extensive testing would be required to ensure that ratings obtained did provide an accurate assessment. It was determined that the time spent on developing a ratings approach would not add significant value to the overall methodological approach and as a result all assessments are left to the methodology participants on a case-by-case basis. There is still the potential for developing a ratings approach as a repeatable means of reaching decisions would be beneficial. Any system would have to be relatively simple as it has been noted that users do not have the time nor inclination to go through anything beyond simple mathematical procedures.

7.6.3 Brainstorming

Plant concepts aim to meet as many of the process and business drivers as possible. No particular means have been suggested for generating concepts in the PI methodology, though some guidelines are given. A creative problem solving session by means of the brainstorming technique (Section 3.2) is one potential approach, with the Challenging technique from the INSIDE methodology Tool B (Section 3.3) also applied to improve the original concepts. A proper structured approach along these lines could be developed for the methodology, detailing the role of the team members and setting out the procedures that should be followed during the sessions.

7.6.4 Software

The potential for converting the methodology from a paper-based to software-based methodology has been considered. It is possible that the knowledge elicitation, blockers and rate limiting stages could be operated with the aid of an information storage system containing all of the checklists. Concepts Generation of concepts could be approached with the aid of a knowledge based system (KBS) which models the thinking procedures taken by an expert in a field to come up with solutions. However, these systems have a weakness in only being able to suggest what is already known,

when the methodology case studies in Chapter 4 have shown that innovation may be required. In addition, there is currently limited information available on the performance of a wide range of PI technology, meaning any KBS would be very restricted in what it could suggest. As a result, the use of a KBS for the PI methodology was not examined further.

7.7 THE PROTOCOL EQUIPMENT

The laboratory protocol investigation in Chapter 5 resulted in the design, construction and testing of a vessel to model the performance of PI equipment in the laboratory. A number of aspects of the equipment that require redesigning to increase its practicality and widen potential applications have been identified and are discussed below.

7.7.1 Heat Transfer Limitations of the Equipment

The protocol vessel currently has no heat removal capability. A redesigned vessel is required which at the very minimum can remove the heat generated within the vessel as a result of the mixing energy input, allowing isothermal operation of non-exothermic reaction schemes over longer time periods. As many industrial reactions are exothermic in nature, a vessel design that is capable of removing potentially significant amounts of heat would widen the applicability of the protocol approach. Constructing the vessel of glass is one means of improving heat removal through the vessel walls, though consideration of other means of removing heat is required.

7.7.2 Additive Volume

The vessel includes a chimney that acts as a liquid seal and allows addition of a small volume of liquid, to a maximum of approximately 10ml. If the chimney was any larger, a significant proportion of the vessel contents would not be subject to proper mixing. Industrial reaction schemes may require addition of proportionally larger volumes of

feed, so a redesigned vessel should allow higher volumetric additions. A floating lid that rises with the increasing volume in the vessel could be utilised. This would need a seal around the impeller shaft and feed pipe to prevent escape of liquid or entrainment of air. For situations when larger amounts of feed are added, the mass present in the vessel would increase significantly over the feed time. As a result, if a constant mixing speed was used, the turbulent energy dissipation rate per kilogram of fluid would be appreciably higher at the start than at the end. A profiled impeller speed could be utilised to ensure equal power input to the liquid over time, or a constant impeller speed could be used that provides the mean mixing energy input over the addition timescale.

7.7.3 Other Applications of the Protocol Vessel

The vessel has been tested with a single liquid phase azo-coupling reaction scheme in this work. Operation with other phases would be beneficial for it to become a widely applicable experimental unit. An independent study is using the protocol vessel with a liquid/liquid scheme to simulate the operation of rotor-stator mixers. The protocol vessel was selected for the study as it is the only laboratory equipment capable of providing sufficiently high turbulent energy dissipation rates. The timescale of the liquid/liquid experiments does not allow for the results to be included in this thesis. Issues relating to the modelling of gas/liquid processes have not been examined in any detail, though it may be feasible to disperse gas underneath the impellers. Solid/liquid systems could also be handled, though solid size would be limited by the small size of the vessel. Other issues relating to solid/liquid mixing have not been examined.

The protocol vessel has been used to test the mechanical stability of a polymer product, as described in Case Study 2 in Section 4.8. A further application has been to a foodstuffs project to examine the effects of mixing on the quality of a product. High mixing speeds were not required here, but the vessel was used due to its homogenous mixing environment.

Use of the protocol vessel in situations additional to this work illustrates the usefulness

of the vessel as a generic type of laboratory equipment over and above its intended use as a means of demonstrating the application of PI. Modelling rotor-stator performance in the independent liquid/liquid mixing study also shows that there is the potential to expand the protocol approach to model different kinds of PI equipment in addition to static mixers, particularly if multi-phase systems can be handled.

7.8 FURTHER REQUIREMENTS

7.8.1 PI Equipment Database

The case studies in Chapter 4 generated only a narrow range of PI plant concepts, usually involving a continuous plant comprising of static mixers and heat exchangers. This demonstrates that many of the selected concepts will be ones in which the methodology participants have personal knowledge and experience. To widen the number of potential options, a database of PI equipment is required to describe what is currently available.

A database should include information on existing PI equipment types and operating capabilities. This would prevent existing possibilities being overlooked. A flowchart approach could be utilised along the lines of that developed by Myers *et al* (1997) for static mixers to show the conditions under which particular types of equipment operate. However, any database can only suggest what is already known and the best solution may depend upon development of novel equipment, rearrangements and new combinations of equipment, or simple modifications to existing equipment. This drawback is similar to the problems facing the application of a KBS to the PI methodology (see Section 7.6.4). PI equipment databases are currently under development elsewhere, in particular within the Britest project (Borland, 1997) and therefore this issue is not explored further here.

7.8.2 Capital Cost Estimations

A major part of the justification for building a PI plant is the cost saving. This requires procedures for estimating the capital cost of a PI plant to allow comparisons to the equivalent cost of more conventional plant. Available cost estimation techniques are based upon conventional plant which may not apply to PI plant due to different relationships between each aspect of the total cost, for example civil engineering requirements which are lower for the much smaller PI plant.

7.8.3 Final Choice

Final choice of whether to retain the existing, conventional plant or build a new plant based upon the concept generated by the PI methodology depends upon a magnitude of economic, timescale and risk factors. Some aspects for consideration are included in the methodology, but it has been decided not to develop this section further as it is outside the objectives of this research which was to generate suitable plant designs. The final decision on whether to progress with a PI plant will be made by someone not involved in the methodology study, though the methodology outline can be used to present all of the information required for the decision in a clear, structured manner.

7.9 FUTURE WORK

The discussion above has highlighted the stages of the methodology which have the potential for further development to widen its applicability and usefulness. These aspects that should be considered in the future are summarised below.

Applications

Expand the issues relating to development of new chemical processes, starting with identification of synthesis routes, to make the methodology an overall tool for process development. This may involve adding to procedures being developed by other

researchers rather than developing a completely novel approach.

Methodology Format

The PI methodology is currently a paper-based tool. Incorporation of software procedures may prove beneficial to its application, particularly for information storage and retrieval. Means of doing this should be considered.

Checklists

The Knowledge Elicitation, Examine PI Blockers and Identify Rate Limiting Features sections include checklists that have been compiled over the duration of this project. These checklists should not be considered as exhaustive as it is likely that other issues will arise during industrial projects. Any such issues should be added to the methodology as and when they occur.

Reaction Kinetics

Knowledge of reaction kinetics is required to determine the feasibility for intensification. Experience has shown that often knowledge of the kinetics is not available. Simple means of examining kinetics are included in the methodology, though further work is required to set out detailed procedures for determining kinetics.

Rate Limiting Features

Identifying rate limiting features of the current process depends upon the participants determining the causes of poor process performance from the available information. There is no structure showing how to go about this, requiring one to be developed.

PI Feasibility Assessment

Procedures for identifying the feasibility for intensifying the chemical process are currently limited to a list of suggested points for consideration. A structured set of procedures would be beneficial.

Concepts Generation

Development of the procedures and keywords is required for a 'brainstorming' approach to concepts generation and challenging of these concepts to achieve the best possible design. Access to a PI equipment database is also required to identify the type of equipment that is available for achieving specific performance..

PI Plant Costing

Comparison of PI plant concepts to a conventional plant requires an estimation of the plant capital costs. Current plant cost estimations are based upon conventional plant and may not apply to PI plant. Means of estimating the cost of PI plants should be investigated.

Laboratory Protocol

Further developments for the laboratory protocol relate to both experimental investigations and equipment design.

i) Design, build and test an improved laboratory protocol vessel to allow closer simulation of real-life operations. Heat recovery capability is required to control temperature for operation over longer time periods and/or with exothermic reactions. The ability to allow the addition of more equal flow ratios of reactants is also necessary.

ii) Full characterisation of the improved vessel, including determination of the impeller flow number and means of estimating the mesomixing lengthscales.

iii) Improved experimental techniques to reduce the experimental errors.

iv) A wider investigation into means of predicting the performance of static mixers through the use of the protocol vessel. This should develop procedures that can be confidently applied to the design of a range of static mixer types, reaction concentrations, reaction schemes and viscosities.

v) Potential for running processes other than single phase liquid.

vi) Potential for simulating PI equipment other than static mixers.

7.10 WALPOT PROCESS INTENSIFICATION METHODOLOGY

A recent publication by Walpot (1999), mentioned in Section 3.6, uses a tool named OPTION, to generate means of introducing innovation and intensification into the design of fine chemicals processes. Walpot's methodology is summarised below, along with comparisons to the PI Methodology, described in Chapter 6 and published in conference papers included in Appendix D. Appendix D.1 was published in October 1997, Appendix D.2 in November 1998 and Appendix D.3 in October 1999 in the same conference proceedings as the Walpot paper.

Stages of Walpot's methodology are compared to the PI methodology in Table 7.1 below. Very little additional information on the content of each section of the approach is given by Walpot.

Table 7.1 Comparisons between the Walpot and PI methodologies

Walpot methodology stages	Equivalent PI methodology stages
Determination of the company's objectives and incentives for PI.	Determine the business drivers.
Analyse the present process, including kinetic studies where the rate of reaction would not be disturbed by limitations in mass transfer.	Knowledge elicitation through the chemistry and plant audits. Running experiments with rapid mixing to remove mass transfer limitations and determine kinetics formed the basis of the laboratory protocol.
Gathering of process conditions and thermodynamic properties to find the rate limiting steps. This involves rate limiting physical and/or chemical steps.	Identify process operating conditions in the audits and then use these in the 'Identify Rate Limiting Steps' section which includes mechanical (physical) and chemical rate limiting steps.
Selecting the issues that have high potential for realisation of the objectives.	Identify the process drivers that, when met, will allow the business drivers to be achieved.

Walpot methodology stages	Equivalent PI methodology stages
Ranking these opportunities.	The PI methodology specifies that drivers should be ranked to prioritise those which the plant concepts should meet.
Generation of innovative ideas in relation to the selected opportunities through the brainstorming technique.	Generate concepts to meet the drivers, potentially utilizing the brainstorming technique.
Ranking of obtained options.	Select the best concept.
Laboratory scale experiments for proof of principle.	PI laboratory protocols.
Pilot plant for proof of technology.	Pilot plant option in the PI methodology.
Full scale design and construction.	Full scale design and construction.

The outline procedures presented by Walpot can easily be translated and represented as the PI methodology framework, with a few differences. In particular, Walpot suggests that only opportunities for intensification are considered and does not have the equivalent of the Examine PI Blockers stage to look for aspects that may prevent PI being applied. Examining the PI blockers is an important stage in the PI methodology as this allows means of overcoming any identified blockers to be considered, potentially further increasing the opportunities for intensification.

The fact that other approaches to PI are now being published demonstrates that PI methodologies are indeed needed in industry. Similarities between Walpot's work and the PI methodology provide an independent validation that the PI methodology has considered the important considerations in the correct manner. Inclusion of additional aspects such as the Examine PI Blockers and Initial Concepts stages increases the usability of the PI methodology over the ideal procedures presented by Walpot.

7.11 FEEDBACK AND JUSTIFICATION

Application to case studies has shown that the PI methodology is capable of greatly

assisting in all aspects of PI projects from initial knowledge gathering through to plant concept generation. Comparison with the independent work of Walpot (1999) also justifies the approach taken. Presentation of the methodology to industrialists throughout the duration of this research, including the conference papers in Appendix D, has elicited positive feedback in the methodology objectives, approach and content. The PI methodology has been stated to meet industry's requirement for procedures for aiding engineers in the design of PI plants (Industrial Communication, see Appendix A).

The laboratory protocol technique has been presented both separately and as part of the overall methodology. Feedback has been received stating that it is a very useful tool that at least prompts consideration into the effects of mixing and meets the need of modelling PI operation in the laboratory (Industrial Communication, see Appendix A). At the time of writing, the laboratory protocol approach is receiving interest from an industrial producer as a means of determining the feasibility for intensifying chemical processes.

The PI methodology has therefore achieved its objective of producing usable procedures and guidelines for examining the feasibility for intensifying a chemical process and assisting in the design of a PI plant.

7.12 CONCLUSIONS

A methodological approach to process intensification (PI) has been developed that sets out the main decision procedures for designing a PI plant. Such procedures are otherwise lacking in industry, forming a barrier to PI as potential users do not know how to approach the design of a PI process, even if knowledge and willingness to apply it exist. The focus of this work is on reactor intensification as the reactor is at the heart of the chemical process and any improvements made here will benefit the entire plant. PI results in smaller, safer, cheaper and more energy efficient plant and it is expected

to play a significant role in the future of the chemicals industry.

The approach required to design a second generation plant to replace one that is not functioning as efficiently as desired was identified as the area that will benefit most from a PI methodology. Consequently, the methodology was developed for this scenario. The methodology intends to identify the most appropriate plant for a process and does not force PI upon situations where it is not really required. Issues relating to development of new processes, starting with generation and selection of the chemical synthesis route, are also discussed within the methodology to show how PI can be considered at the earliest possible stage.

PI is achieved by designing the plant to meet the needs of the process. The PI methodology identifies the process needs through process and business drivers. Process drivers are the characteristics of the chemical reaction scheme that determine the performance the plant should deliver, whilst business drivers ensure that the economic requirements and benefits desired from a new plant are assessed, forming much of the justification for applying PI. Business drivers are set at the commencement of a project, though additional ones may arise as the project progresses.

Chemistry and plant audits gather all the required information through a checklist approach and allow assessment of the feasibility for intensification. Key aspects of the chemistry audit, in addition to those items normally gathered during process development, are determination of reaction kinetics and examination of mixing effects on a chemical reaction scheme. Reactions with fast reactions are particularly feasible for intensification, whilst improved mixing is how PI achieves many of its benefits.

The plant audit reviews the existing plant, identifying any reasons why it is not operating as efficiently as it could and providing information to assist in the design of a new plant.

Following identification of the drivers, the methodology sets out the procedures for design of an appropriate plant. It was found that plant concepts can occur throughout

the methodological approach and the tendency to favour these options potentially suppresses the generation of superior concepts. An 'Initial Concepts' stage is included in the methodology to encourage any such concepts to be noted down and considered in the proper manner once all the drivers are known, thereby allowing the best plant design to be achieved.

A laboratory protocol has been devised and developed to overcome the existing inability to model PI in the laboratory. Failure to determine the performance of reactions in PI equipment means the benefits of PI are not identified and therefore an intensified plant may not be considered. Protocols are applied during the chemistry audit to assist in determining the feasibility for intensification, and then later to demonstrate plant concepts and aid in design of the full scale or pilot plant.

A specifically designed stirred vessel utilizing semi-batch addition that is capable of providing a wide range of mixing conditions is used for the protocol. No previous applications of stirred vessels to simulate continuous operation have been found in open literature. An investigation into the laboratory protocol approach has shown that it is possible to use the protocol vessel for simulation of operation in static mixers. Additionally, the vessel has been used in two independent projects due to the high mixing energy inputs and good mixing uniformity achievable, demonstrating its usefulness as a generic piece of laboratory equipment. The laboratory protocol investigation has provided the basis for a strong experimental technique that, incorporated within the overall methodological approach, can increase the likelihood of PI application and all the benefits that this can achieve.

The PI methodology has been applied to four industrial case studies which serve to justify the approach taken whilst aiding in the development of the content. Applying the PI methodology improved procedures, with a particular benefit being reduction of the project timescale. Feedback has been received from industrialists stating that the methodology, including the laboratory protocols, does indeed provide the required procedures for the application of PI.

A change in the way process development is traditionally approached is necessary for process intensification to be properly adopted and applied. This PI methodology provides a mechanism to promote such a change by encouraging PI to be considered where it is normally overlooked.

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APPENDIX A
INDUSTRIAL COMMUNICATION

The references to 'Industrial Communication' in this thesis relate to situations when knowledge cannot be attributed to one particular source. This includes matters arising out of group discussions and occasions when the same opinion was voiced by a number of people. All the sources who have contributed to the knowledge presented in this thesis are acknowledged in this appendix. Members of the Britest project are listed in Section A.2, whilst participants in Case Study 4 in Chapter 4 are listed in A.3.

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A.2 BRITEST PROJECT PARTNERS

The following are the original members of the Britest - Batch Route Innovative Technology Evaluation and Selection Techniques - project.
Supported by EPSRC (Engineering and Physical Sciences Research Council) and IMI (Industrial Manufacturing Initiative)

J.Borland (Project Manager)

Glaxo Wellcome
ICI
Jacobs Engineering
Rhone-Poulenc Chemicals
Zeneca

ICSTM Imperial College of Science, Technology and Medicine
Leeds University Business School
UMIST University of Manchester Institute of Science and Technology

SOCSA Speciality Organic Chemicals Sector Association
Member companies are:
Bush Boake Allen
FMC Process Additives
Hampshire Chemicals
Holliday Dyes & Chemicals
MacFarlan Smith
Pentagon Chemicals
Robinson Brothers
Synthetic Chemicals

A.3 PARTICIPANTS IN CASE STUDY 4

Britest Process Intensification Workshop. Held at BHR Group Limited, 13th May 1999, Cranfield, UK.

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APPENDIX B

AZO-COUPLING REACTION SCHEME

This appendix outlines the azo-coupling reaction scheme and the procedures by which the turbulent energy dissipation rate within a vessel can be determined. Full details of the reaction scheme, calculation procedures and computer programs are given by Baldyga and Bourne (1999), Hearn (1995) and Pearce (1998).

A solution containing both 1- and 2-naphthol is used as the bulk reactant, with a solution of diazotised sulfanilic acid being the additive. 1-naphthol (A) reacts with diazotised sulfanilic acid (B) to yield two monoazo isomers (R and T) which can both react further with B to form a single bisazo dye (S). 2-naphthol (C) couples to give a single monoazo dye (Q). All reactions compete for diazotised sulfanilic acid. At a temperature of 25°C and pH 9.9, the rate constants of the extended scheme obtained by Bourne *et al* (1992), are:

$$A + B \rightarrow R \quad k_{1\text{-}p} = 12238 \pm 446\ m^3mol^{-1}s^{-1} \tag{B.1}$$

$$A + B \rightarrow T \quad k_{1\text{-}o} = 921 \pm 31\ m^3mol^{-1}s^{-1} \tag{B.2}$$

$$R + B \rightarrow S \quad k_{2\text{-}o} = 1.835 \pm 0.018\ m^3mol^{-1}s^{-1} \tag{B.3}$$

$$T + B \rightarrow S \quad k_{2\text{-}p} = 22.25 \pm 0.25\ m^3mol^{-1}s^{-1} \tag{B.4}$$

$$C + B \rightarrow Q \quad k_3 = 124.5 \pm 1.0\ m^3mol^{-1}s^{-1} \tag{B.5}$$

Temperature has to be maintained at 25°C during the experiments. Sodium carbonate and sodium hydrogen carbonate are used to buffer the solution to a pH of 9.9.

Yield of byproduct Q, X_Q provides the basis for determining the mixing characteristics of the reactor. X_Q is defined as:

$$X_Q = \frac{C_Q}{C_R + C_T + C_Q + 2C_S} \tag{B.6}$$

C_i is the final concentration of species i after the reaction is complete. Spectrophotometry is used to determine the concentrations of each product in a sample. The Beer-Lambert law links the measured absorbency of a compound at a particular wavelength to its concentration, its molar absorption coefficient and the length of light path through the measurement zone. Bourne *et al* (1992) have determined the molar absorption coefficients of the dye products over the range 390-700 nm, at an interval of 10nm. This data is valid for solutions with an ionic strength of 444.4 mol/kg, requiring the addition of a sodium carbonate and sodium hydrogen carbonate buffer solution to the experimental sample. A diode array spectrophotometer (Hewlett Packard HP 8452A) was used to measure the absorbency of each sample and therefore determine the product distribution. The associated error of the analysis is ±0.005 in X_Q.

A mass balance is performed to provide a check on the experiments. As reported by Pearce (1996), assuming that no unknown side reactions occur, a mass balance, MB, on the sulfanilic acid, B, is given by:

$$MB = \frac{C_{BO}}{\beta(1+\alpha)(C_{R+T} + 2C_S + C_Q)} \qquad \textbf{(B.7)}$$

where α is the volumetric ratio of (A+C) to B, and β is a dilution factor introduced from buffering the collected sample to an ionic strength of 444.4 mol/kg. A mass balance of ± 5% is considered to show reliable results.

Product distribution from azo-coupling experiments is dependent upon: the ratio of the kinetic rate constants; the stoichiometric ratios of the reactants; the volumetric ratio, α, of bulk A and C to additive B; the Damkohler number, which is the ratio of the mixing to chemical reaction timescale. For the azo-coupling reaction scheme the Damkohler number is:

$$\overline{Da} = \frac{k_{2\text{-}0}\, C_{BO}}{E\ (1\ +\ \alpha)} \qquad \textbf{(B.8)}$$

C_{BO} is the initial concentration of unmixed diazotised sulfanilic acid. The engulfment

rate coefficient E is the inverse of the micromixing timescale derived in Equation 2.13. The operating mode and bulk flow pattern of the reactor (e.g. continuous plug flow or back-mixed semi-batch) will also affect the yield. Reactor flow patterns are accounted for by discretising the feed addition. For continuous addition, the feed is effectively added as one drop. For semi-batch addition, discretising the feed into 20 separate drops, each of which is assumed to react to completion before the next drop is added, will give results of approximately the same accuracy as experimental measurements.

Figure B.1, reproduced from Hearn (1995), outlines the procedures for determining energy dissipation rates using the engulfment micromixing model and experimental results. These procedures assume that the reaction is micromixing limited.

FORTRAN programs have been built to run the micromixing models. The one used for this research was developed by Pearce (1998) and is known as 'INTERZONE2'. Figure B.2 shows the input file required by the program. Given the concentrations and volumes of reactants, and the turbulent energy dissipation rate present within the system, the program calculates the product distribution through the procedures given below:

1. Add a drop of reactant B (initial concentration C_{BO}) to a solution containing A and C. The drop size is depends upon the operating mode. For continuous operation the feed is treated as only one drop. For STR operation, 20 drops are used.

2. The drop of B becomes the reaction zone, which spreads exponentially by engulfment.

$$\frac{dV_{ei}}{dt} = E V_{ei} \qquad \textbf{(B.9)}$$

Where V_{ei} is the volume of the reaction zone, t is the age of the reaction zone and E the engulfment rate.

3. The rate of engulfment E is controlled by eddies of a certain size and is determined from:

$$E = 0.058\left(\frac{\epsilon}{\upsilon}\right)^{1/2} \qquad \textbf{(B.10)}$$

4. The concentrations can be found in the reaction zone having first determined the concentration in the surrounding environment. This is done by solving

$$\frac{dC_i}{dt} = E(\langle C_i\rangle - C_i) + R_i \qquad \textbf{(B.11)}$$

C_i = reaction zone concentration of species i

$\langle C_i\rangle$ = environment concentration of species i

R_i = rate of production or consumption of species i

There is one equation for each species. These equations are solved in dimensionless form by a fifth order Runge-Kutta method until the required conversion of B in the reaction zone is achieved. The following dimensionless variables are used:

$T = Et$ dimensionless time

$C_i = C_i/C_{BO}$ dimensionless reaction zone concentrations

$\langle C_i\rangle = \langle C_i\rangle/C_{BO}$ dimensionless environment concentrations

β_{ij} = (rate constant of reaction)/(rate constant of slowest reaction)

Da = Damkohler number (Equation B.8)

Therefore

$$\frac{dC_i}{dT} = \langle C_i\rangle - C_i + Da\sum\beta_{ij}C_iC_j \qquad \textbf{(B.12)}$$

5) Add the next (j^{th}) drop, updating the environment conditions for the j^{th} drop, using

$$<C_i>_j = \frac{<C_i>_{j-1}(\alpha\sigma + j - e^{\tau}) + C_{i,T}\, e^{\tau}}{\alpha\sigma + j} \qquad \textbf{(B.13)}$$

where e is the base of natural logarithms. The program keeps track of the reaction zone volume through Equation B.9. Self-engulfment is accounted for by slowing down the rate of engulfment depending on the size of the reaction zone relative to the total volume. Termination occurs when conversion of the additive, B, has reached a value input by the user.

To experimentally determine the turbulent energy dissipation rate in a vessel, the steps below are followed:

1) Run the experiments under micromixing controlled conditions and take samples.
2) Analyse samples through spectrophotometry to determine product distribution and final yield of Q, X_Q.
3) Run the micromixing model, inputting the experimental concentrations and volume ratios at a range of ϵ values. This will produce a graph of ϵ vs X_Q.
4) Read off the appropriate value of ϵ at the experimental value of X_Q.

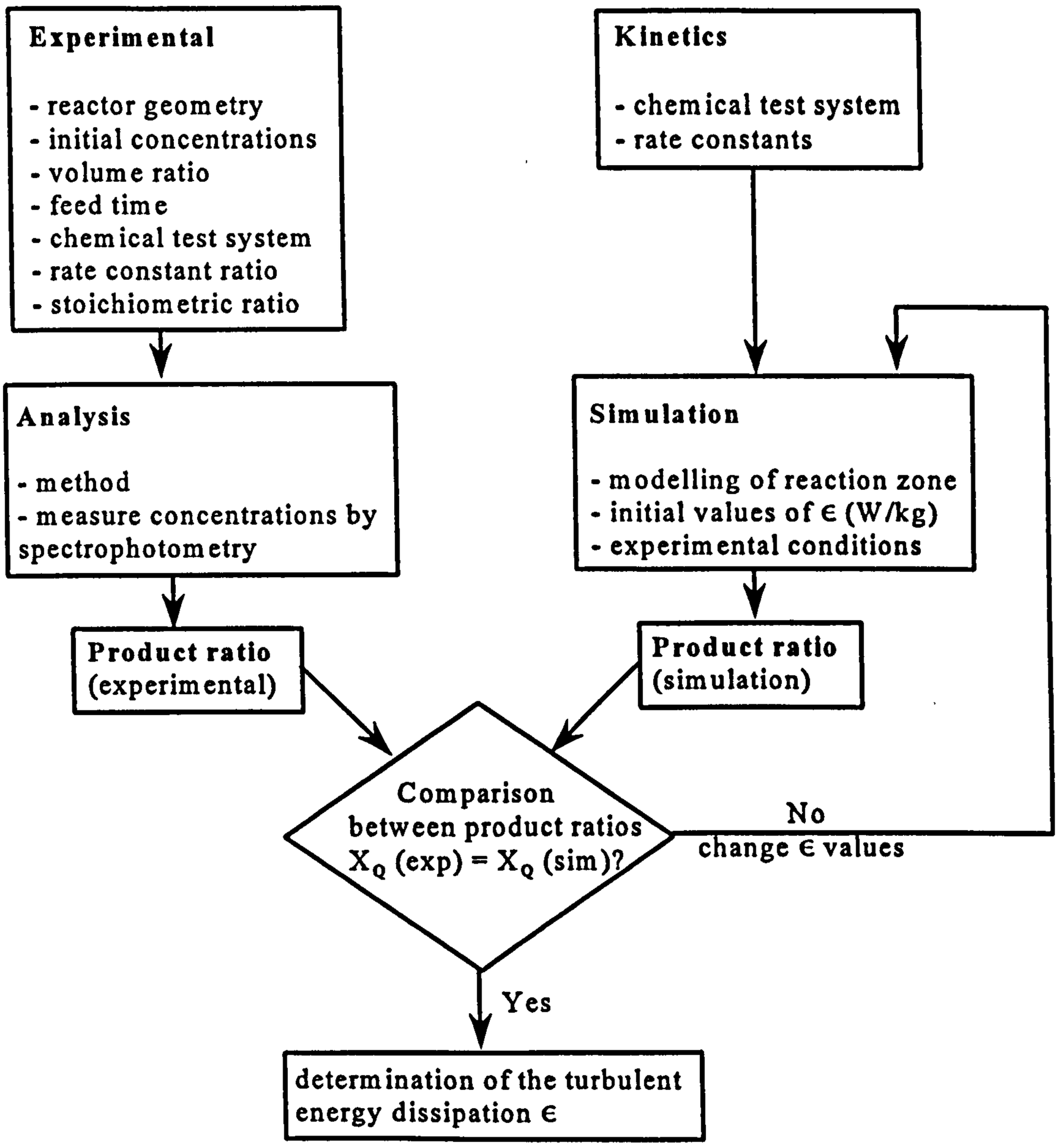

Figure B.1 Determining turbulent energy dissipation rates through a combination of experiments and modelling from Hearn (1995)

*** Engulfment micromixing model (with self-engulfment)
*** Azo coupling reaction scheme ***

1) A + B ---> R k1p=12238.0 m^3/mol s
2) A + B ---> T k1o=921.0 m^3/mol s
3) R + B ---> S k2o=1.835 m^3/mol s
4) T + B ---> S k2p=22.25 m^3/mol s
5) C + B ---> Q k3=124.5 m^3/mol s

A = 1-naphthol B = diazotized sulphanilic acid C = 2-naphthol
R = para isomer T = ortho isomer
S = competitive consecutive dye product Q = competitive parallel dye product

1) Initial B concentration (mol/m^3)?
2.5
2) Initial molar ratio of A to B (-)?
1.5
3) Initial molar ratio of C to B (-)?
6
4) Discretise feed into how many drops (-)?
20
5 Ratio of environment volume to total drop volume (-)?
150
6) Number of epsilon values (-)?
(epsilon = turbulent kinetic energy dissipation rate (W/kg))
1
7) Values of epsilon (W/kg)?
100
8) Fractional conversion of B in each drop (-)?
0.999
9) Dynamic viscosity of reaction zone (Ns/m^2)?
8.9e-4
10) Density of reaction zone (kg/m^3)?
1000
11) Desired accuracy of solution (-)?
1e-3
12) Initial dimensionless time step size (-)?
1e-3
13) Maximum number of steps for each drop (-)?
90000

Figure B.2 Input file for FORTRAN model of azo-coupling reaction scheme

APPENDIX C

IMPELLER FLOW NUMBER DETERMINATION

The flow number of an impeller, also known as the pumping number, is a measure of the amount of fluid passing through the impeller at a given rotational speed. A flow number value is required for the impeller system in the laboratory vessel to estimate the local velocity of liquid and hence aid in calculation of the characteristic mixing timescales.

For the purpose of the laboratory protocol investigation in Chapter 5, the impeller flow number has been estimated from previous work. The main source of information is the work carried out by Musgrove (1996) examining the effect of impeller size and configuration on flow number.

The protocol vessel uses twin three blade pitched blade turbines with an impeller diameter to tank ratio, D/T, of 0.6. Spacing of the impellers is 33mm, or 0.55D. The trends on impeller number from changing the number of blades, impeller diameter, number of impellers and impeller to tank diameter are determined from literature and used to estimate the flow number for the protocol vessel impellers.

Flow number versus number of blades.

Three test results are available for 155mm diameter pitched blade turbine (PBT) impellers with 2, 4, and 6 blades and 45° blade angle, shown in Table C.1. A dished vessel with diameter of 310mm was used, hence D/T=0.5.

Table C.1 Effect of number of impeller blades on flow number

Number of blades	Flow number
2	0.62
4	0.73
6	0.81

The relationship between the number of blades and measured flow number is approximately linear. From this information, the flow number value for a 3-bladed impeller can be interpolated. The value obtained is 0.67.

Flow number versus impeller diameter

Two geometrically similar 4-bladed PBTs with D/T=0.5, have been tested, with results shown in Table C.2. Assuming a linear relationship between impeller diameter and flow number, a value of fl for D=60mm, which is the diameter of the protocol impellers, can be obtained through extrapolation. This gives a value of 0.95 for a 60mm diameter impeller.

Table C.2 Effect of impeller diameter on flow number

Impeller diameter	Flow number
104 mm	0.85
155 mm	0.73

Flow number for dual impeller arrangement

A dual impeller configuration has been tested to examine the effects of the configuration, measured in terms of the spacing between the impellers. The PBT used had a flow number of 0.9 in solitary operation. It was found in the experimental study that the lower impeller had a lower flow number than the upper impeller, though the values have been averaged in Table C.3.

Table C.3 Effect of impeller spacing on flow number

Impeller spacing	Flow number
0xD (single PBT)	0.90
1xD	0.85
1.25xD	0.81

The relationship is a curve, which is used to estimate a value of fl = 0.88 for the protocol vessel dual impeller spacing of 0.55.

D/T versus flow number

The ratio of impeller diameter to tank diameter affects the flow number of the impeller. A chart produced by Hills (1995) shows flow number decreasing as D/T increases from 0.25 to 0.5. D/T for the vessel is 0.6, which is outside the data range. However, an estimation has been made that the flow number is 0.55 at D/T=0.6, compared to fl=0.6 at D/T=0.5, shown in Table C.4.

Table C.4 Effect of D/T relationship on flow number

D/T	Flow number
0.25	0.87
0.3	0.79
0.4	0.68
0.5	0.6

Estimation of flow number

An estimation of the protocol vessel flow number can now be made. The approach taken is to base the value upon a 104mm diameter 4-blade PBT, which has a flow number of 0.85, and make corrections for number of blades, size, spacing and vessel diameter ratio. This is achieved by obtaining the ratio of the corrected flow numbers in each of the above sections to the base case impeller.

The flow number correction factors are:

Blades Ratio for a 3 blade turbine to a 4 blade turbine = (0.67/0.73)

Diameter Ratio for a 60mm diameter compared to 155mm diameter = (0.95/0.85)

Spacing Ratio for dual impeller spacing of 0.55 compared to single impeller = (0.88/0.9)

D/T Impeller to tank diameter ratio of 0.6 compared to 0.5 = (0.55/0.6)

Therefore

$$fl = 0.85 x [(blade) x (size) x (spacing) x (diameter\ ratio) correction\ factors]$$

$$fl = 0.85 \ x \ (0.67/0.73) \ x \ (0.95/0.85) \ x \ (0.88/0.9) \ x \ (0.55/0.6)$$

The protocol PBT flow number is hence calculated to be 0.78.

This value can only be regarded as an estimation, though inspection of the flow number for other impeller systems suggests that this value is representative of the size, type and configuration of the protocol impeller.

APPENDIX D

PUBLISHED PAPERS

D.1 METHODOLOGIES FOR PROCESS INTENSIFICATION

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BIIR Group Limited

Paper presented at the 2nd International Conference on PI in Practice, 21-23 October 1997, Antwerp, Belgium.

ABSTRACT

Process Intensification (PI) can be considered to be a design philosophy where the fundamental requirements of a chemical process are analysed, and process plant designed which match the precise needs of the process and meet the business needs.

A range of PI technologies is available or under development, which when correctly applied could provide significant business benefit. However, most have been developed and presented to industry using a technology-driven approach. This has limited the application so far. The outline methodology presented in this paper takes a business/process driven approach to PI. Its application is demonstrated on an existing industrial process.

Key words: process intensification, methodology, heat exchanger-reactor, spinning disk reactor

1. INTRODUCTION

The philosophy and technology behind PI have been in existence for several years, but despite benefits which include smaller, cheaper and inherently safer plants (1) with improved product quality, uptake is still very low. One significant reason for this is conservatism within the chemical industry resulting in unwillingness to take the risk with novel technology. The general feeling is that companies want to be the second or third to use a new technology, but never the first, resulting in PI equipment being untested at commercial scale operation.

There is still a lack of awareness of PI in industry, which is another major reason for the low uptake. Chemical Engineers are not usually taught about novel technology in any detail, so they only know how to design conventional plants. Chemists have little knowledge of process engineering and many design the chemistry to be carried out in batch stirred tank reactors which are well understood, with proven reliability and performance.

Applications for PI equipment are currently sought with a technology driven approach. The novel technology that does exist is developed by organisations who have knowledge of one or maybe two types of equipment. This means that when the organisations are confronted with a problem or are looking for applications, their approach will be on the basis of trying to make the process match their particular

equipment, rather than choosing the equipment to match the process as would ideally be done.

The ideal approach is driven by process and business requirements. Process drivers are those where the physical and chemical requirements of the process are determined and then used to select the equipment which best suits the process. Business drivers are financial issues relating to the operability and profitability of the process.

The challenge of increasing the use of PI lies in producing methodologies capable of promoting a different approach to process development. Past considerations or applications of PI technology have had a largely unstructured approach meaning time was not spent as efficiently as was possible. This paper sets out a development methodology by means of which process intensification is brought into consideration for upgrades of existing processes. Ideally the methodology would be applied right from the initial stages of a new process, including involvement in the selection of the synthesis route, as this is where opportunities for the application of PI are missed. This complete methodology will use many of the ideas expressed in this paper.

2. BACKGROUND

For a new process the chemist traditionally identifies a number of chemical synthesis route options. The most promising ones are then identified for further analysis. By the time the engineer gets involved the synthesis may already have been developed to the stage where it can only be done in conventional plant, usually batch or semi-batchwise in stirred tank reactors (STRs). Very often engineers are not given sufficient data on the kinetics of the synthesis to consider whether the operation could be intensified, even if they do have knowledge of PI (2,3).

The engineer should get involved earlier in the project and encourage the chemist to develop faster reactions, or not slow down intrinsically fast reactions. Slow reactions are preferred in STRs as they are easier to control. Inhibitors can be added to slow reactions down to allow the study of the reaction steps, but then continue to be used for the full scale operation as the reaction scheme has been shown to work. Some synthesis routes could be discarded which would have been ideal for PI but not possible with conventional equipment, as intensified equipment is capable of handling very fast, exothermic reactions.

3. PI METHODOLOGIES

The methodologies described below form sections of the overall PI methodology. They represent a relatively 'coarse screen' which can be used at a very early stage of process development to identify the potential benefits of a PI approach. More detailed methodologies could be used at later stages for specifying particular equipment. Figure 1 shows the outline decision process which the overall methodology follows.

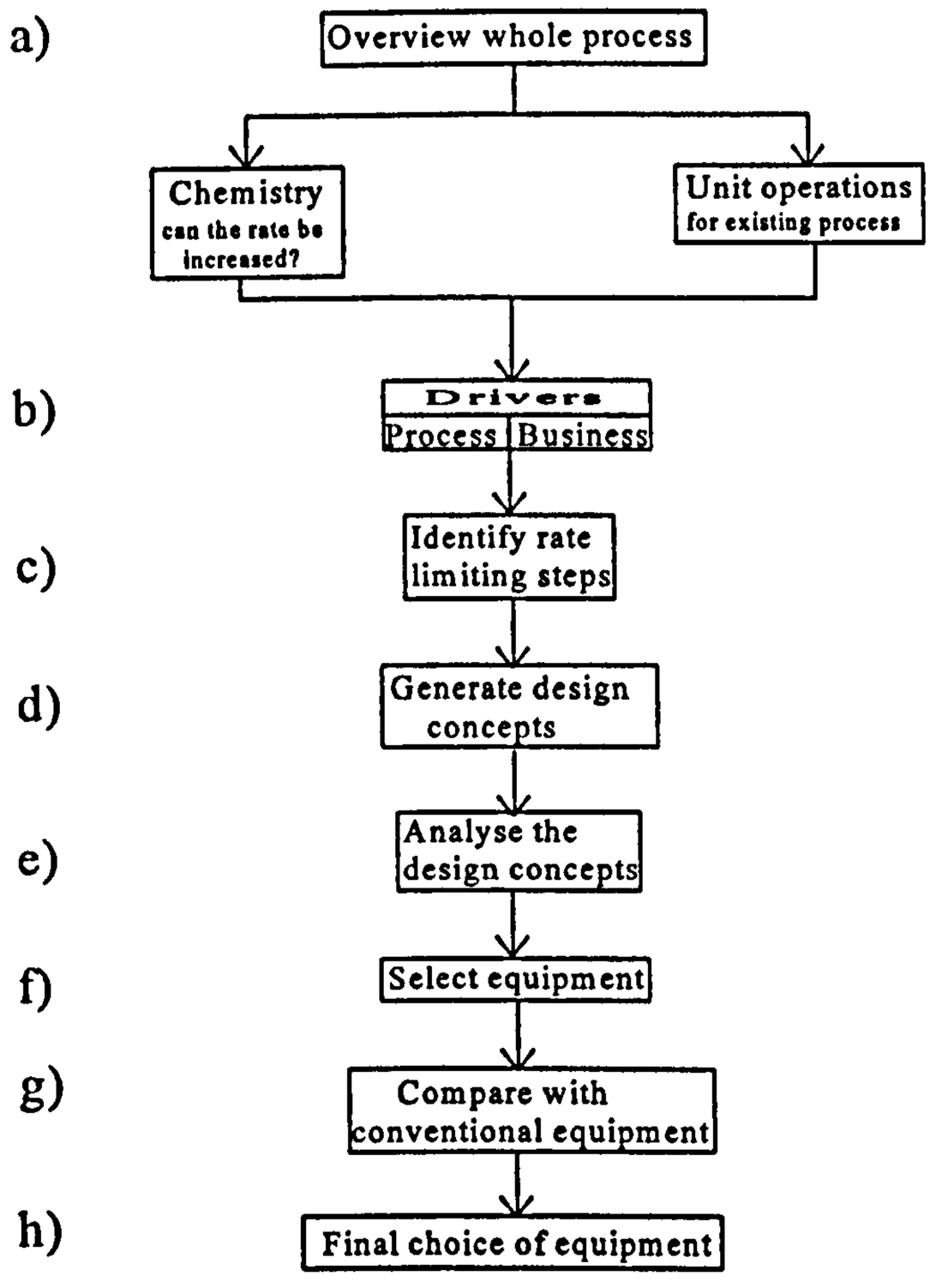

Figure 1
Overall PI Methodology

3a) Understand whole process

The first step is to develop an understanding of the whole process and appreciate how each aspect affects the others. Chemists and engineers should work together from this stage onwards until the full scale development begins. It is much less likely that information or possibilities will then be overlooked. The approach will be split into two areas:

i) Chemistry
ii) Unit operations in existing (conventional) production plant

i) Chemistry

The chemist should explain the chemistry of the synthesis route and why any particular solvents/catalysts are used. The question has to be asked "can the reaction be made faster?" as it is possible that chemists have not explored this possibility as slow, easily controllable reactions are preferred when using STRs. Even if a particular chemical synthesis route has been selected as the best one for the manufacture of a product, there still may be the potential to use different solvents or catalysts.

An important idea for the application of PI is to assume that intensified equipment can cope with any reaction and conditions. For example heat transfer in intensified equipment is far superior to that which can be achieved in STRs, enabling very

exothermic reactions to be run at or closer to their maximum rate. Following this assumption will allow all synthesis possibilities to be explored and evaluated against each other. Some reactions may eventually prove too extreme for any kind of equipment, though others will be considered in more detail which would otherwise have been discarded.

If the kinetics of the synthesis route are not known then factors such as the mixing sensitivity and speed of the reaction have to be determined. One approach is to use laboratory protocols which are currently being developed. The protocols will be a sequence of small-scale experiments designed to extract the required information.

The 'S' curve (figure 2) is used to demonstrate how the performance of a process is affected by the mixing rate. For reactions to run at their inherent kinetic rate, the mixing rate has to be faster than the rate of reaction. If this is not the case, the reaction will be running slower than is theoretically possible, thus reducing the process performance as by-products have more opportunity to form.

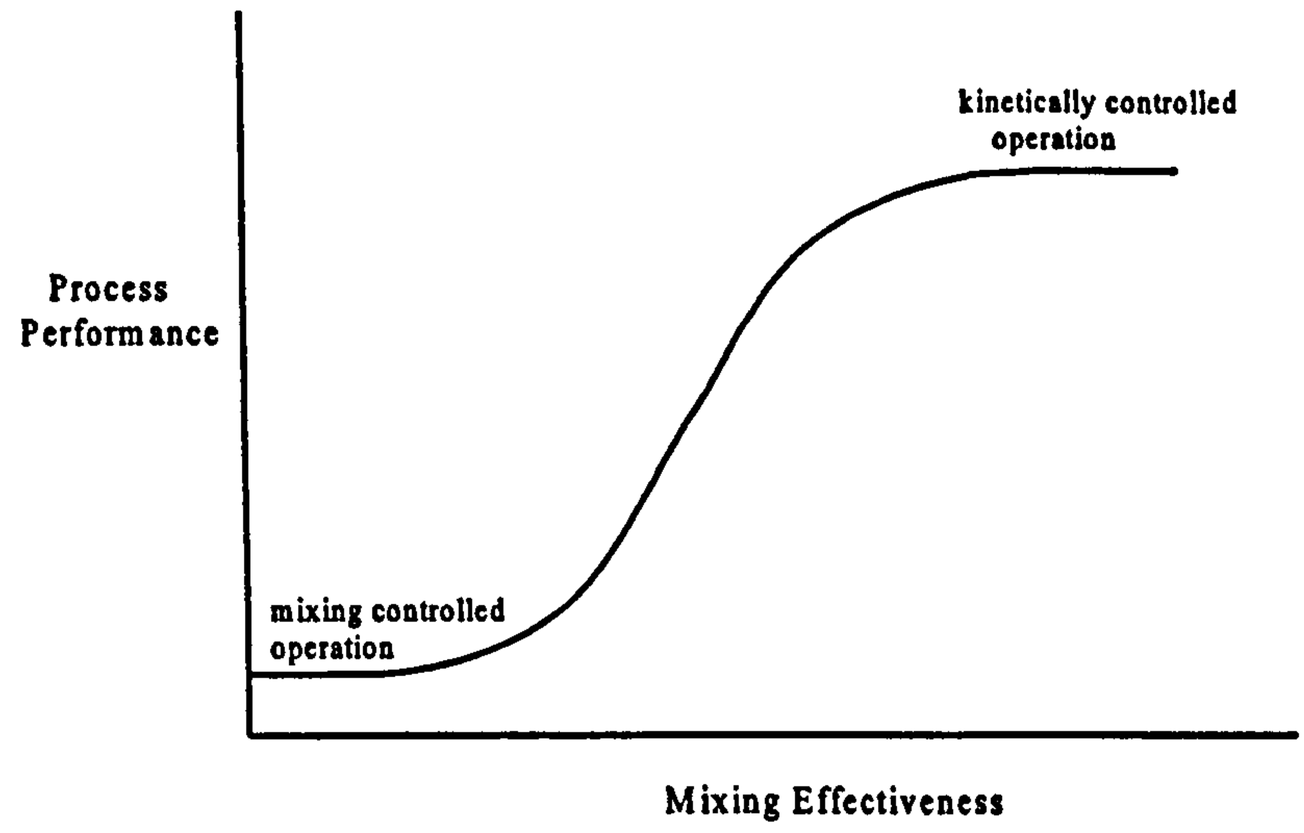

Figure 2. 'S' curve of process performance

Process performance could be a measure of yield, selectivity or other measurable factors relating to product quality. Fast reactions running under poor mixing conditions, such as in STRs, will operate in the lower part of the s-curve. Improving mixing will move the operation to the right and up the curve, but it may not be possible to reach the upper levels of the curve using conventional equipment. Using PI could be the only way to achieve operation at the top of the 'S'-curve.

ii) Unit operations in existing process

The existing conventional process is examined to determine the operating capabilities of each unit and why it is being used. Appreciation of the mass and heat transfer capabilities for each unit will be needed. This is to compare the existing equipment to what the process actually requires and determine whether the current equipment is fully suited to the job. Any issues relating to the required flexibility or reusability of the plant will be covered here as these could be important reasons as to why particular equipment was chosen.

3b) Drivers

For a project to be given the go-ahead to start, the major drivers will already be known and fully considered. These could include the need to improve environmental performance or reduce costs and will mainly be business drivers. Business drivers are economic and social considerations relating to profitability. These could include pressure from HSE and/or new legislation to make the plant safer or cleaner, batch processing times, product quality and capital available.

The study of the process which forms the initial part of the methodology will identify all the other important drivers which will mainly be process drivers. Process drivers lie in optimising factors such as mixing, heat transfer and mass transfer within the system. These will have the effect of making the process more efficient and possibly reducing downstream costs. Examples are, poor conversions and safety problems from by-products

These drivers will show where attention has to be focused in the plant. PI is one way to achieve some, if not all, of these drivers by means of reducing inventories of dangerous materials and improving yields and conversions. The flexibility and reusability required from the equipment in a particular process could become an important business driver as some PI equipment has to be tailored to the process, thus reducing flexibility.

3c) Identify Process Limitations

The limitations of the existing process can be identified from the results of the analysis of the equipment and chemistry by comparing the kinetics of the synthesis to the capabilities of the equipment. The position of the current operation on the 'S'curve will show how much scope there is for improvement.

The optimal operating conditions, expressed in terms of the ideal required heat transfer and mixing, are then produced, expressed in terms of a 'process envelope' which is the range of conditions under which the reaction will perform best (4).

3d) Generate Design Concepts

A 'brainstorming' session should be held in which concepts for achieving the optimal operating conditions are suggested. A database of all PI equipment available and its capabilities is required here so that no possibilities are overlooked. If the development team following the methodology are not aware of the existence of a particular piece of kit then they may go into the equipment driven mode by trying to match the limited range of equipment they have knowledge of to the process. A knowledge-based system could be implemented which holds a database of all equipment. This would assist in the decision making process by providing 'plant envelopes' which are the range of conditions the equipment is capable of operating under.

3e) Analyse the Design Concepts

All the ideas suggested previously must then be analysed to study how each of them fits the requirements of the process and matches the drivers. The synthesis of the reaction could be looked at again with hindsight to improve the kinetics if this is practicable.

There may be factors which limit or rule out the use of a particular piece of kit, such as having solids with large particle sizes and concentration, or the presence of very viscous materials.

3f) Select Most Suitable Equipment

The results of the analysis will be used to select the equipment and approach most suitable for the task. This could be either intensified or conventional equipment as this methodology is not about forcing PI onto situations where it is not really required. If one particular process cannot immediately be decided upon, the options should be subject to more detailed consideration against each other to select just one. This will require costing methodologies which are not as readily available or developed as those for conventional processes.

3g) Compare With Conventional Equipment

Due to the conservatism in the chemical industry towards novel technology it may be necessary to fully justify the choice of an intensified plant. If PI is a possibility and the process could still be done in conventional plant, a full comparison will have to be made between the two, focusing mainly on performance and economics. Any major safety or environmental improvement from using PI will be of importance.

3h) Final Choice of Plant

Once the comparison has been made between PI and conventional, the person or team responsible for making the ultimate choice of plant equipment should have an open mind to the use of PI. This final decision process involves factors which are outside the scope of this basic methodological approach, such as risk of using novel equipment, legislation and lead time to commissioning of plant. A high risk factor and long lead time to commissioning may rule out the use of the PI approach even though significant financial and operability benefits have been shown to exist.

The methodology concept will now be illustrated by application to a typical bulk chemical process.

4. APPLICATION OF PI METHODOLOGY

Aldehyde Oxidation Process

The process is the partial oxidation of an aldehyde (5). The existing plant operates satisfactorily at the moment and another plant is to be built to increase capacity. The question is whether to build another conventional plant like the existing one, or use novel, intensified equipment. The analysis was been based on limited process information but still demonstrates how PI might be applied to a broad class of reactions, showing how the methodology operates. The PI concepts presented are not intended to be a recommendation on how the process should be done, but are there to illustrate how the methodological approach can identify possibilities that would otherwise be overlooked.

4a) Overview Whole Process

i) Chemistry

The generic process under consideration was

$$R.CHO_{(l)} + \tfrac{1}{2}O_{2(g)} \xrightarrow[\Delta H]{\text{initiator}} R.CO_2H_{(l)} \qquad \Delta H \sim -350 kJ\,mol^{-1}$$

Typical reactants are liquid aldehydes with air or pure O_2. The initial reaction is gas-liquid mass transfer controlled and the whole reaction scheme has the potential to become very fast.

ii) Equipment

Currently, oxidation of aldehydes to organic acids is carried out at elevated pressures and moderate temperatures in a recycle reactor that is fitted with gas dispersion equipment. Figure 3 is a basic flowsheet of the process.

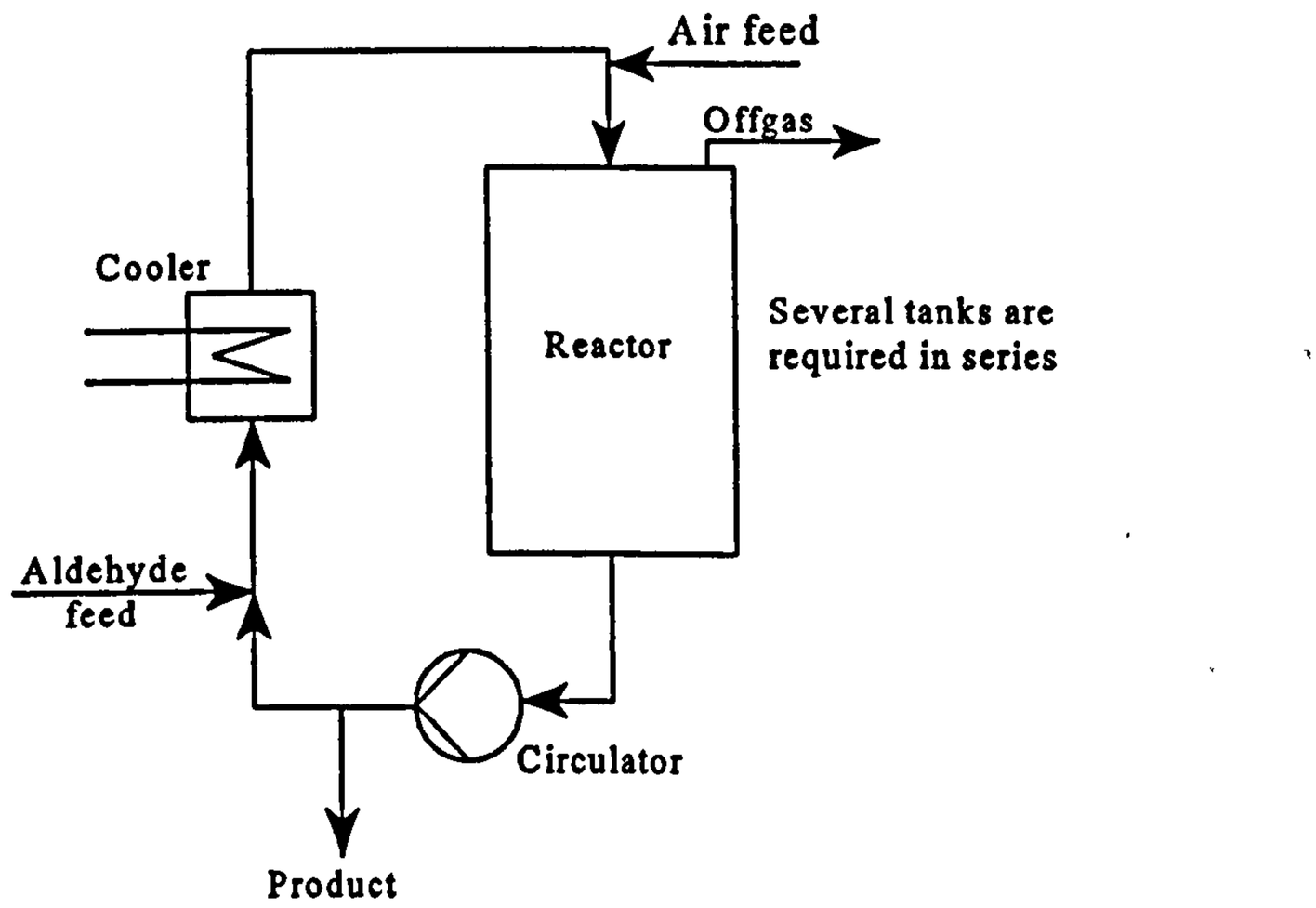

Figure 3. Aldehyde oxidation flowsheet

An external heat exchanger is used for temperature control. It is often necessary to have several large tanks in series to achieve high conversion of the aldehyde. Vessel size and circulation rate are determined by the need to achieve the required mass transfer whilst keeping liquid velocities low in the vessel so gas is not entrained in the loop.

4b) Drivers

There are several reasons for wanting to improve the existing plant.
The business drivers are:

- Desire to increase capacity/productivity
- Improved safety
- Reduction in manufacturing costs
- Lower energy consumption
- Reduction in size of plant

Currently there are several problems with the traditional g/l tank reactor which are classed as process drivers due to the need to optimise the actual chemical process occurring in the equipment.
The process drivers are:

- byproduct formation (coloured material, organics)
- organic peroxides formed cause safety problems
- unconverted raw material
- Cooling must be reliable to prevent the occurrence of a runaway reaction.

4c) Identify Process Limitations

- mass transfer of air/O_2 into liquid aldehyde
- heat transfer out of vessels
- liquid velocity in tanks has to be low to prevent gas being entrained in the loops

These limitations are then used to produce the ideal operating conditions in the 'process envelope' which can be quantitative if sufficient data is available, e.g. mixing power dissipation required, or maximum inventory of reacting materials. Ideal conditions include using O_2 rather than air and raising temperature and pressure to increase the speed of reaction

4d) Generate Design Concepts

Equipment with good mass and heat transfer capabilities is needed that is also capable of handling the gas, which currently restricts the operation of the stirred tanks.
Preheat reactants to reaction temperature to minimise the required reactor volume.
Move to a continuous reactor (with the necessary heat and mass transfer capability) rather than the current loop-continuous system.

The above 'plant envelope' can then be compared against the capabilities of both conventional equipment (STRs) and PI equipment to identify all possible equipment options.

4e) Analyse the Design Concepts

The importance of all the above process requirements and equipment options were considered and two PI approaches were proposed. These are both discussed below.

4e.1) Integrated Chemical Reactor-Compact Heat Exchanger (6)

The reaction and heat transfer are integrated by carrying out the oxidation reaction in a gas-liquid compact heat exchanger (CHE). Figure 4 shows the outline flowsheet.
Advantages of this include:

- Mass and heat transfer capabilities allow continuous production with pure oxygen.
- Can cope with raised temperatures and pressures (up to 300°C and 400 bar).
- Heat of reaction is removed as it is generated. Fast reaction is controllable, so by-product formation is reduced.
- Reduced inventories of reacting material make the equipment inherently safer

4e.2) Spinning Disk Reactor

The high centrifugal acceleration of liquid films on a rapidly spinning surface provides

high mass and heat transfer coefficients (figure 5) (7,8). Excellent mixing occurs in thin, wavy, highly sheared films of liquid which can be enhanced by irregularities, such as grooves, on the surface of the disk. Transfer rates can be controlled through the rate of rotation of the disk.

4e.3) PI Plant Flowsheet

The basic plant flowsheet is the same for both reactor options, with the spinning disk reactor (figure 5) replacing the heat exchanger-reactor in figure 4.

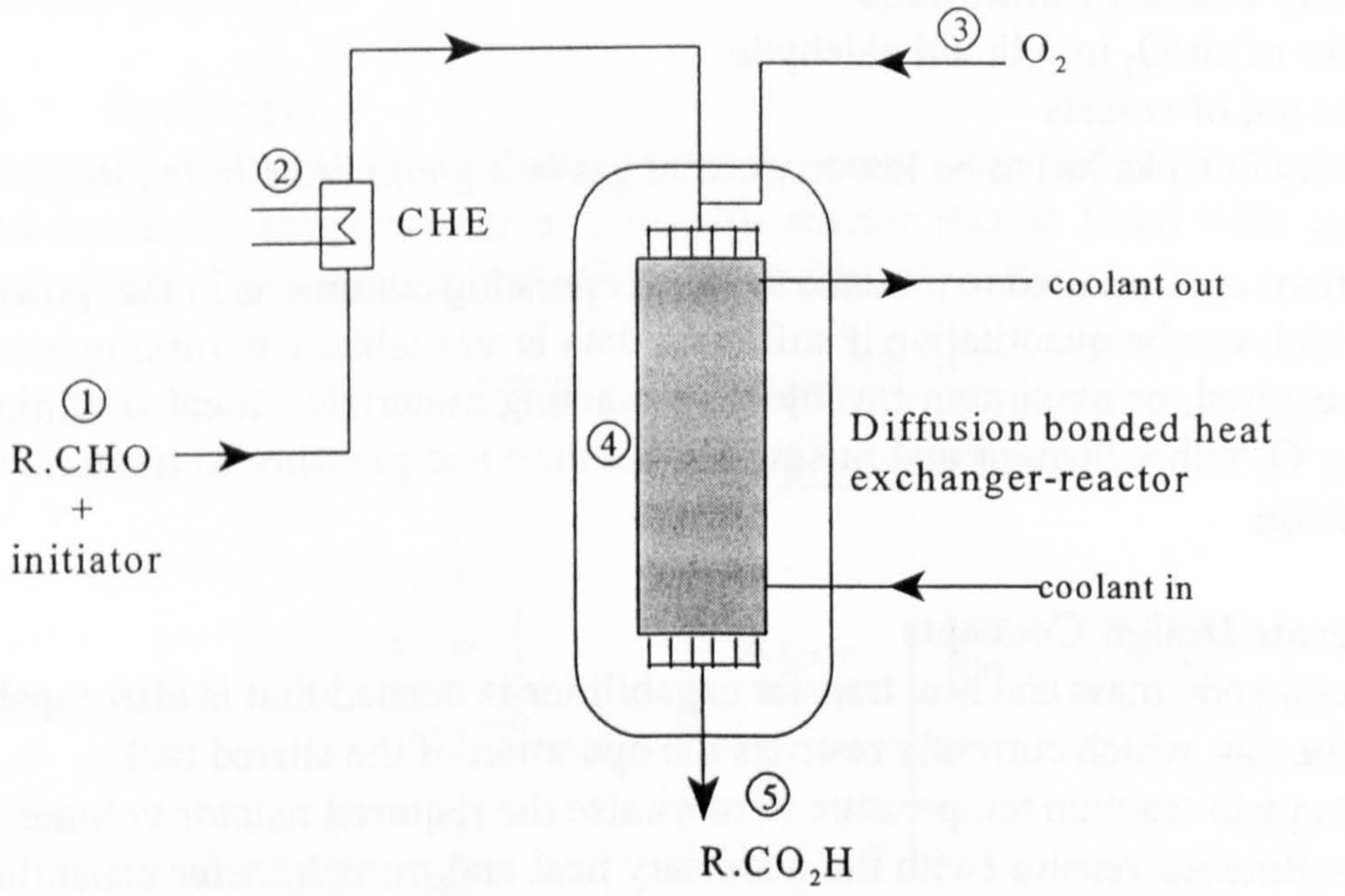

Figure 4. CHE-Reactor flowsheet

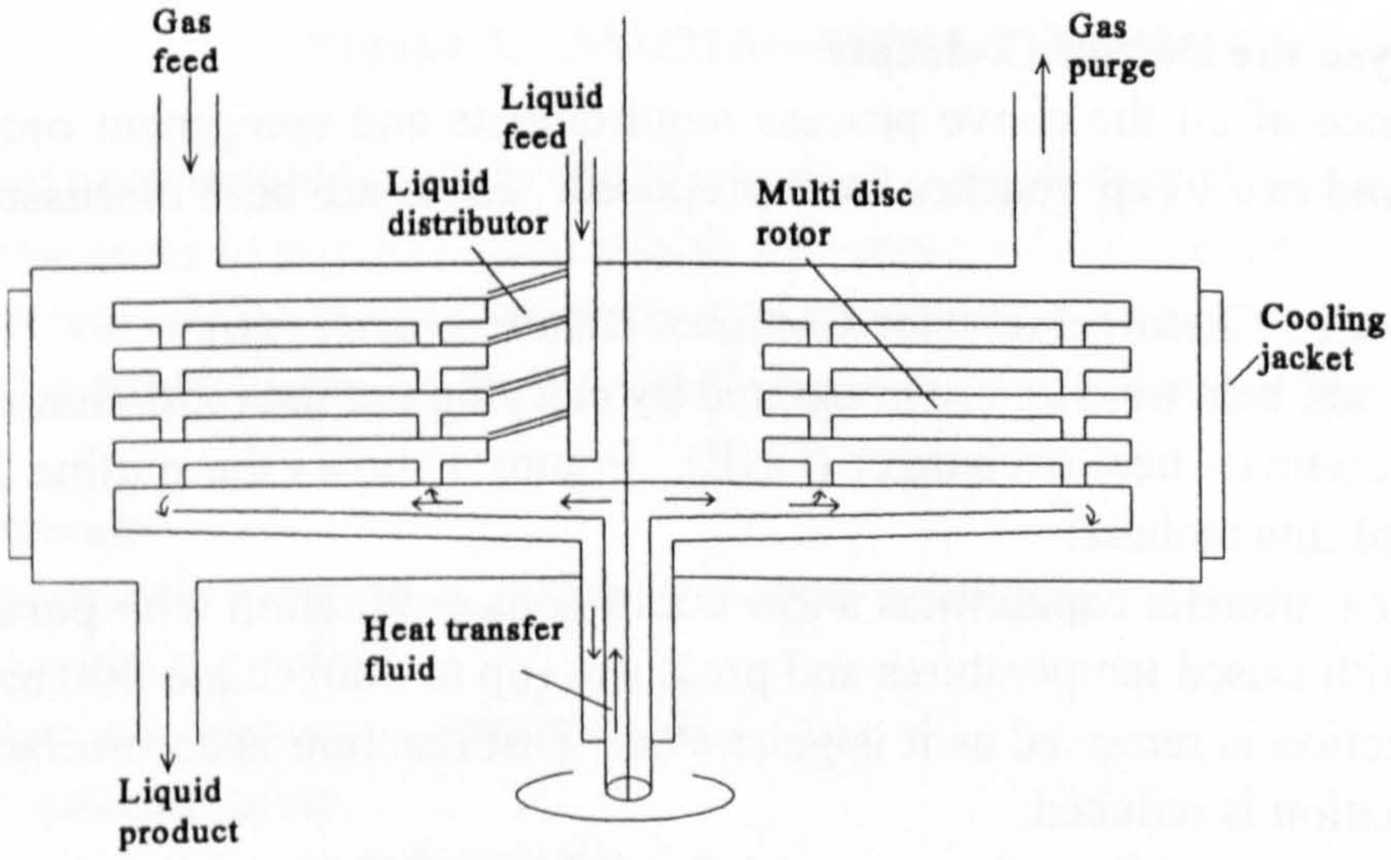

Figure 5. Schematic rotating disk reactor

Stages

1. Liquid aldehyde and initiator pumped into the flow line under pressure
2. Liquid aldehyde preheated to initiation temperature (free radical formation)
3. O_2 fed into aldehyde feed manifold at inlet of heat exchanger-reactor
4. Exothermic reaction is controlled in diffusion bonded heat exchanger-reactor
5. Carboxylic acid is collected from the outlet manifold of the heat exchanger-reactor

4f) Select Most Suitable Equipment

The two possible intensified options have to be compared against each other, choosing just one as a potential process. This will require a full costing and operability analysis.

4f.1) Heat Exchanger Reactor

The major item here is the heat exchanger itself. It is estimated that 200m^2 of surface area is required. Cost estimates for such units are very difficult to assess, but a figure £100k for the capital cost of the unit is considered reasonable. By comparison, a conventional plate heat exchanger of the same surface area would only cost £13k. Pump and compressor costs are likely to be low due to the small flow (2.5l/s), despite the higher pressure, and are estimated to cost £30k. As PI units are relatively expensive for their size and weight, the installation factors are expected to be lower than for conventional plant. A factor of 3, compared to the conventional 5, is assumed, giving a total plant cost of £390k.

4f.2) Spinning Disk Reactor

Estimates of capital costs are very difficult to make, but the spinning disk bears a closer relation to a pump than more complex centrifuges. If a 'safety factor' of 4 is assumed, this gives an estimated cost of £100k. This cost is considered realistic if such units become readily available, though costs may be more for a one off. The compressor cost will be comparable to the conventional unit (£15k) but pumping costs would be very low. The installed cost (factor of 3 again) is £345k, comparable to that of the heat exchanger-reactor.

4g) Compare with Conventional Process

Compare the intensified process selected in (f) to a conventional process, which has been calculated to cost £745k. This is approximately double the cost of the intensified plant.

Other Benefits of PI:

Product Purity:	Removal of the heat of reaction as it is produced will lead to less degradation, and therefore less coloured byproducts. Elimination of hot spots will also improve product quality.
Safety:	Likelihood of thermal runaway is reduced. Inventories are 2-3 orders of magnitude smaller than the conventional process.
Energy Use:	The 150kW circulatory pump in the existing plant will be eliminated. Continuous units will produce a steady stream of

high grade heat, which might be more readily utilised/recovered (estimated to be 9 MW).

4h) Make Final Decision

All aspects of the decision making process will be brought together here to decide upon the best possible option. The PI aspect should be approached with an open mind. The plant being built here is a dedicated plant, so flexibility will be less of an issue than for normal, refusable batch plants, though potential reuse of the equipment once this plant has been decommissioned has still to be considered.

5. FUTURE WORK

The work outlined in this paper is still in the early stages of development and is expected to evolve into a generic methodology applicable to all aspects of process development. The case study considered is an existing process, though the options raised are only initial thoughts on what could be done. The methodology will require testing on a commercial development to show whether the format will work in practice.

The laboratory protocols, which are an integral part of understanding the chemistry and the requirements of the process, have been identified as the key area for the success of this methodology. These protocols have to produce the right results to enable the rest of the methodology to proceed. Research into the experiments required is underway.

This PI methodology should be complementary and compatible to other process development assessments, such as safety, environmental hazards and economic issues. Recommendations from each of the studies will need weighting accordingly, and this will have to be examined in the research. Access to a database of the capabilities of all equipment, intensified and conventional, will be needed to assist in the selection of equipment for the process.

6. CONCLUSIONS

The overall methodology described in this paper operates as a decision route for considering PI during process development, starting with an existing plant and chemical synthesis. It prompts engineers to get involved in the decision making process far earlier to ensure opportunities for developing a safer, cheaper PI plant are not missed. Chemists will be encouraged to do the right experiments to determine kinetics and mixing sensitivities of the reactions, providing engineers with information to match equipment to the process requirements.

This approach is not about forcing PI upon situations, as it may not be the most efficient way of achieving the process/business targets. An inappropriate and unsuccessful application of PI could have negative consequences by further strengthening the conservatism towards it. The case study is an example of how PI could be applied to an industrial process, showing there to be considerable benefits in using novel

equipment, though this is only from an initial view of the plant.

This methodology is intended to be only one part of the overall decision procedure for selecting process routes. A dramatic change in the way of thinking within many organisations and in the way development is traditionally done will be required for this approach to be fully effective. In order to implement PI, awareness of it has to be raised in industry and this methodology is one means of introducing the concept of PI where it may normally be overlooked.

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D.2 A METHODOLOGICAL APPROACH TO PROCESS INTENSIFICATION

M.Wood and A.Green

Paper presented at the IChemE Hazards XIV Symposium, Manchester, 11th November 1998.

Process Intensification (PI) is a design philosophy where process plant is designed to match the fundamental requirements of the chemical process and meet business needs. The benefits of applying PI include smaller, inherently safe plant; reduced energy requirement; improved product quality; lower capital cost. This paper describes a methodology that assesses the feasibility for applying PI to a chemical process. Application of the methodology is demonstrated on the design of a continuous, intensified reactor to replace a semi-batch stirred tank reactor. The resulting conceptual PI plant has an inventory three orders of magnitude smaller, eliminates runaway potential, and provides significant economic benefits.

Keywords: Process intensification, static mixer, compact heat exchanger, continuous process

INTRODUCTION

It is likely that the chemical plant of the future will be far smaller than that of today (1). This can be achieved only by a step change in the plant technology used, rather than incremental improvements of existing plant items. The philosophy of size reduction has been in existence for several years under the name of Process Intensification (PI). Smaller equipment can result in reduced capital cost and reduced operating costs, whilst giving improved product quality. Just as important, according to Kletz (2), is that smaller often means inherently safer. Despite these benefits, uptake of PI appears to be low. There are many possible reasons for this. Standard process design and development has stressed the use of batch reactors (3), often with limited available knowledge of reaction kinetics. Lack of awareness of novel technology has to be overcome, from new graduates right through to top level management. Conservatism within the chemical industry may also result in unwillingness to take the risk with novel technology. The challenge of increasing the use of PI lies in promoting a different approach to process development, which should assist in overcoming these barriers.

Current procedures for applying PI technology also need to be considered, as this can tend to be done with an equipment driven approach. Organisations that have developed novel technology will look for applications where a chemical process can be run in their particular equipment. The equipment driven approach can be summed up through the opinion that PI is currently a solution looking for a problem. This situation needs to be reversed so problems look to PI for solutions, known as the process driven approach. Equipment should be chosen to match the process and allow it to run at its

optimal rate, resulting in the consideration of a range of intensified equipment where normally only conventional plant would be used. The methodology set out in this paper uses a process driven approach to assess the feasibility for applying PI. It should be stressed that this methodology is not about forcing PI upon situations where it is not really required, but it aims to find the best solution for running a process. Improved understanding of the process as a result of the methodological approach can lead to benefits even if it is shown that full PI is not feasible.

PROCESS INTENSIFICATION (PI)

PI has been categorised as follows by Hannon and King (4):

a) Equipment - reducing the size of a unit operation. Full PI uses novel equipment to reduce size by 2-3 orders of magnitude, improving the process safety. Intensification can also apply to reducing the size of a conventional unit through more efficient operation.
b) Physical - combining two or more operations in one unit. Examples include pumps as mixers and reactive distillation. Compact reactor-heat exchangers, described by Edge *et al* (5), are an example of both equipment and physical intensification.
c) Chemical - improving the reaction scheme. Using different reagents or catalysts can improve yield or speed reactions up. Fast reactions are preferable for PI as they require shorter residence times and lead to smaller equipment.
d) Plant - Size reduction of the entire plant and integration of utilities to save energy and space.

PI can be applied across the whole flowsheet, but for the purpose of this work the focus is on the reactor. Any changes or improvements made here will affect the entire plant. The reacting inventory is often the most dangerous on the plant, as shown by Barton and Nolan (6) in a study of thermal runaway incidents. Reducing this inventory through the use of PI would be a major aspect in improving the safety of the process. Although PI has many benefits, there can be some potential drawbacks, such as lack of flexibility. PI equipment usually has to be tailored to a particular reaction scheme, whereas stirred tanks can run a number of chemical process, increasing plant occupancy and hence perceived value for money. To improve flexibility, a standard framework of feed pipes can be envisaged with interchangeable intensified reactor units to suit different reaction schemes. Not every reaction scheme can be intensified.

The 'S' curve (fig.1) is used to demonstrate how process performance is linked to plant performance. Factors under consideration for plant performance might be the mixing or mass transfer rate or heat transfer capability, while process performance might be yield of desired product, energy efficiency or product quality. Plant performance can be illustrated through the mixing sensitivity of some reaction schemes. For reactions to run at their inherent kinetic rate, the mixing has to be faster than the rate of reaction. If this is not the case, the reaction will be running slower than is theoretically possible, increasing residence time and reducing the process performance as by-products have more opportunity to form. Ideally operation would be close to the top of the S-Curve without moving too far to the right, which would entail excessive costs. PI can be the only means of improving plant performance enough to move up the

S-Curve. The interaction between PI and chemistry is also shown. Improving chemistry (for example with a more selective catalyst) can push performance up to a higher S-Curve, but benefits will be lost if operation is lower down this S-Curve.

Removing reactor mechanical limitations to allow reactions to run at their inherent kinetic rate can be achieved by utilising a range of PI technology (7). In-line devices such as static mixers, ejectors (fig.2) and rotor stator mixers have proved to be effective as mixers and reactors, with good plug flow characteristics and mixing intensities up to three orders of magnitude greater than stirred tanks. Exploiting intensified force fields is another approach to intensification. Ramshaw (8) has shown that centrifugal fields can be used for separations, reactions, heat and mass transfer. The centrifugal field within a rotating disk reactor (fig.3) creates thinner, unstable liquid films, improving mass and heat transfer. Ultrasonic, electrostatic and magnetic fields can also be used for process intensification (9).

EXISTING PROCESS DEVELOPMENT AND SAFETY METHODOLOGIES

Hazop (10) is a well established safety methodology which is applied once the plant design is reasonably detailed, giving limited opportunity to intensify or redesign the plant for inherent safety. To gain the maximum benefits, it is necessary to consider safety and PI as early as possible in process development. This requires engineers being involved with development chemists to ensure the right chemical characteristics are being looked for. Several methodologies have been published exploring the inherent safety of a chemical process route (11, 12, 13). These include options to consider novel, intensified technology as a means of achieving inherent safety, though it will be necessary to follow a dedicated PI methodology to determine what this intensified plant might look like.

There may be apparent conflicts between PI and inherent safety methodologies, particularly for fast reactions which are most favourable for reactor PI. Slow reactions are preferred in conventional stirred tanks, particularly for exothermic reactions where the rate of heat generation will be limited. This enables the relatively poor heat removal capability of the stirred tank to cope. Fast, exothermic reactions could be considered as less inherently safe, or even completely undesirable from a conventional plant point of view. Hence, both the chemistry and plant need to be considered together to get a full grasp of inherent safety, as intensified plant can open up new, safe operating windows.

THE PI METHODOLOGY

The methodology sets out structured procedures to follow for considering PI during process development. The overall methodology, known as the framework, consists of a number of protocols detailing the information needed to ensure the potential for PI is fully examined. Figure 4 shows the framework which is formatted to apply to situations where an existing chemical plant is to be replaced or upgraded. Each of the methodological steps is described below.

a) Business Drivers

Determine why it is desirable to change the plant. This step is phrased 'business drivers' as these reasons are normally of an economic nature. Safety, health and environmental concerns are increasingly becoming important factors. Even so, these relate back to business issues as it is preferable to achieve these requirements in the most cost effective manner, or by ensuring costly incidents do not occur. Another major business driver may be to have a higher and more efficient production rate. These drivers are required to set targets for the plant design to meet.

b) Knowledge Elicitation

An understanding of the whole process is required which is gained through the knowledge elicitation stage. The approach is split into separate chemistry and plant audits, though there will be interaction between the two.

The Chemistry Audit examines the whole reaction scheme. The potential to use different solvents, catalysts or operating conditions should be considered. Ideal operating conditions and those conditions that promote byproduct formation should be determined, such as temperature of operation or residence time. Check if the chemical reaction rate is inhibited in any way. Some knowledge of the kinetics and thermodynamics of the reaction is essential.

The Plant Audit examines what the existing plant currently does. The audit should include all physical aspects of the reactor, including mixing and heat transfer capabilities, feed rate and position of feed addition. It is necessary to have a fundamental understanding of the reactor to determine where and how the reaction occurs. If the intention is to run a new chemical reaction scheme in existing equipment, as is the case in many fine and speciality chemicals processes, the equipment should be audited as if it were already running the new process.

c) Examine PI Blockers

Blockers are those properties or conditions of a process which may prevent the application of PI. Many are process blockers to do with the nature of the chemicals themselves, such as the presence of solids. PI equipment often has narrow channels, which large solids would not pass through. Fine solids can be handled. There may be some business blockers which relate to practical problems of running PI plants, such as flexibility or continuous operation versus batch production. Batch production is preferred in some sectors of the chemicals industry, such as pharmaceutical manufacture where there is a requirement for batch identification. Consider whether any identified blockers can be prevented or worked around.

d) Identify Rate Limiting Steps

Rate limiting steps are conditions preventing the overall process running at a faster rate. These may be mechanical limitations such as low heat transfer area, poor mixing or limited supply of feedstock to the reactor from an upstream operation. Chemical rate limiting steps, for example slow kinetics or mass transfer into a solid reactant, may occur. Rate limiting steps and blockers are considered in parallel as there can be common elements, such as slow reactions which are both a PI blocker and a rate

limiting step. PI should aim to remove or improve rate limiting steps.

e) Assess PI Viability

The potential for intensifying a process is determined by pulling together the results of the audits, blockers and rate limiting steps into a mid-methodology assessment. This will ensure all the required information has been gathered and properly considered. Even if it is determined that full PI is not possible, it is worth continuing with the methodology as improvements to the conventional plant could be found that partially intensify it.

f) Drivers

Business and process drivers are required to set targets for the plant design to meet. The business drivers identified at the start of the methodology, which are the economic reasons why it is desirable to intensify the process, should be reviewed to keep a clear idea of the overall aims of the project. Process drivers are those characteristics of the chemical reaction scheme that determine the required operating conditions within, and performance of, reactor equipment to allow the process to run at its most efficient rate. A process driver example is the rate of heat release from a reaction determining the heat transfer capability required of the equipment.

g) Initial Concepts

Throughout the methodology, ideas or concepts will occur on how to intensify the process, which will tend to be equipment driven concepts for applying familiar equipment. These ideas should be documented for discussion in the proper manner at the appropriate methodological stage. Accepting an initial concept early on could introduce bias into the rest of the methodology, preventing further, possibly superior, plant concepts being suggested.

h) Generate Design Concepts

A creative problem solving session should be held in which plant concepts are suggested for meeting the process and business drivers. Include the initial concepts in this session. A database of available PI equipment and their capabilities would be useful here so that no possibilities are overlooked, but concepts should not be restricted to plant items already known about. The success of the concepts generation stage depends on thinking laterally to come up with possibly novel solutions to a problem.

i) Select Best Concept

All the concepts suggested must be analysed to study how each of them matches the business and process drivers. There may be factors which limit or rule out the use of a particular piece of equipment, such as it not being available in the required material of construction for corrosion resistance purposes. The best concept must now be chosen. Some economic analysis may be required if there is more than one feasible choice.

j) Laboratory Scale PI Protocols

It will be necessary to prove that the selected concept will work with actual process chemicals. PI laboratory protocols are being designed to demonstrate the performance

of continuous, intensified operation without the need for a pilot plant. This will allow the quantification of any potential benefits of intensification, such as improvement in product quality, shorter reactor residence time and lower reacting inventory.

k) Compare With Conventional Plant

List the strong and weak points of the existing and conceptual plant. Showing that the conventional plant is not fully suitable for a process, due to mechanical rate limiting features, could be just as important as showing the benefits achievable by PI when trying to justify its use.

l) Final Choice of Plant

The person or team responsible for making the ultimate choice of plant equipment should have an open mind to the use of PI. This final decision process involves factors currently outside the scope of this methodology, such as the risk of using novel equipment, legislation and lead time to commissioning of plant. A high risk factor and long lead time to commissioning may rule out the use of PI, even if significant financial and operability benefits have been shown to exist.

PI CASE STUDY

The methodological approach will now be illustrated by a feasibility study recently carried out on a fine chemicals nitration process, which generated an intensified plant concept. The process has a multiple sequence of additions of which only the nitration step was initially considered for intensification. It soon became obvious that the whole process could be intensified.

a) Business Drivers

The potential for a runaway reaction to occur has been identified, emphasising the need for safer equipment. Production needs to be increased. The plant should be relatively cheap to build. Some knowledge of PI does exist within the company and there is a general feeling that continuous, intensified operation is the way forward.

b) Knowledge Elicitation

Chemistry Audit. All of the process steps consist of blending, reaction and heat transfer operations. Reactions in every step are almost instantaneous and some are very exothermic. All reactants are single phase liquid. Solids can exist in the initial stages, though controlling temperature prevents solids formation. The last process stages involve crystallisation, but crystal sizes are small. Byproduct formation for the nitration step at full scale operation (taking 18 hours) is far higher than that in laboratory production tests (taking 4 hours). This shows a PI plant with short residence time could significantly reduce byproduct formation.

Plant Audit. A 13,000 litre glass lined stirred tank (fig.5a) with cooling jacket and coil is currently used. The large reacting inventory is a major safety concern. For the exothermic nitration step, reactant feed is literally dribbled into the reactor over a period of 18 hours to allow the removal of all the heat of reaction. If feed rate was increased for any reason, there is large potential for runaway reaction conditions to occur. Total

batch time for all reaction stages is 30 hours. Low heat and mass transport from the reaction zone at the feed pipe exit could promote byproduct formation.

c) PI Blockers

No particular PI blockers exist. Any solid formation can be controlled. Corrosiveness may become an important issue as a glass-lined stirred tank reactor is currently used to resist the operating conditions. Manufacturing intensified equipment in corrosion resistant materials will increase the cost several times over, but the equipment will still be relatively cheap due to its small size.

d) Rate Limiting Steps

As reaction kinetics are fast, the rate limiting steps are all mechanical. Poor mixing in the stirred tank, which restricts heat transport from the reaction zone, then low heat transfer from the vessel combine to cause the very long feed addition and batch time.

e) Assess PI Viability

The process is suitable for PI due to the lack of blockers and fast, single phase liquid reactions.

f) Drivers

Business drivers are improved safety and productivity at low capital cost. Process Drivers are fast kinetics and high heat release, meaning a plant has to deliver intensive mixing and heat transfer.

g) Initial Concepts

Concepts suggested during the project were based upon previous experience, using an equipment driven approach. These included a heat exchanger loop on the existing reactor, which would improve heat removal and reduce batch time, and a compact reactor-heat exchanger.

h) Generate Design Concepts

For the nitration reaction it is desirable to rapidly mix the reactants and then remove the heat as quickly as possible. From these process drivers, a number of concepts were generated in addition to the initial concepts. These possibilities include utilization of existing PI equipment and some more novel solutions involving new arrangements of existing equipment.

i) Select Best Concept

The concept eventually chosen to achieve the drivers is a static mixer followed immediately by a plate and frame heat exchanger (fig.5b). The reaction will take place in the static mixer, with the adiabatic temperature rise limited to an acceptable level by the presence of inert components from upstream stages. Byproducts formation should be significantly reduced due to the short residence time within the reactor. A similar concept is used for the other reaction stages. There are some novel features of the overall plant design that would not have resulted from an equipment driven approach.

j) Laboratory Scale PI Protocols

A requirement before this project can move into the detailed design phase is demonstration of continuous operation as proof of concept. Experimental procedures have been devised to do this.

k) Compare with Conventional Plant

Figure 5 is an approximate scale drawing of the existing reactor and the conceptual intensified nitration reactor, demonstrating the immense size difference. The PI plant will consist of five reactors, but even so, total inventory is three orders of magnitude smaller than the existing stirred tank. Although a full comparison with the conventional plant cannot be completed until the PI protocols are done, a preliminary economic comparison has been made. The product quality achievable, which would be determined by the PI protocols, is important as it could remove the need for a downstream purification stage with all its associated costs. Major points for comparison are:

	Current	PI	Comments
Production	15 tpa	50 tpa	Increased annual sales value of £2 million, based on continuous operation for two weeks per quarter.
Reacting Inventory	13,000 litres	0.2 litres	Full PI plant inventory (including inter-reactor piping) is approximately 15 litres.
Heat transfer	Poor	Good	Current process feed addition is limited by the poor heat transfer. PI reactor runs stoichiometrically.
Operating safety	High runaway potential	Minimal runaway potential	Runaway conditions should not occur in PI reactor, even if cooling fails, as it is designed to operate adiabatically with cooling after each reaction stage.
Capital cost	£100,000 for new reactor	£40,000 for plant	Cost of control system and other associated items will be evaluated in the next design stage.
Plant layout			PI reactors could literally be bolted to a wall and not require building space as the stirred tank does.
Nitration time	18 hours	0.25s for reaction	Total PI nitration time for reacting and cooling is 3 seconds.
Residence time	30 hours batch time	1 minute	Substantially shorter overall residence time limits the opportunity for byproduct formation

Complexity	4 plant elements	11 plant elements	PI plant is more complex with six static mixers and five heat exchangers required to replace the vessel, impeller, cooling coil and cooling jacket.

Other points under consideration include the filtration stage at the end of the process. Currently this is done batchwise. In order to get the maximum benefit out of the PI process, filtration should be continuous. The cost of installing a continuous filtration system will be examined at the next stage of this project. The alternative is using holding tanks to store product until there is enough to operate the batch filtration step. This would still allow the benefits of improved product quality and safer operation of the PI plant to be achieved. Manual intervention and labour required on the PI plant will be greatly reduced compared to the existing plant.

l) Final Choice of Equipment

The company is reviewing market demand for the product and looking into how the plant can be made in such a way that it can be reconfigured for other products, before deciding whether to replace the existing plant or not. PI laboratory protocols will be followed to fully determine the benefits the PI plant would produce before proceeding onto the production of a more detailed design.

CASE STUDY SUMMARY

Application of the PI methodology has been demonstrated on the conceptual design of an intensified plant for a nitration process, with the methodology acting as a checklist to ensure no important aspects were overlooked. The reasons why the existing stirred tank reactor has a long operation time and high byproducts yield have been identified, showing substantial improvements can be made. Following the methodology generated a PI concept with novel aspects that would not have resulted from an equipment driven approach. Comparison and selection procedures have yet to be completed.

CONCLUSIONS

The PI methodology presented in this paper operates as a decision route for assessing the feasibility for intensifying a chemical process. Consequences of applying PI include smaller, inherently safer plant that is cheaper to build and operate. The methodology is tailored for application to existing chemical processes, though it can also be applied to completely new processes. The methodology is not about forcing PI upon situations, but choosing the best possible plant design to achieve the business targets. Ultimately, integration of this PI methodology with inherent safety methodologies has the potential to produce large financial and safety benefits through enabling effective use of PI.

The case study applies the methodology to an existing fine chemicals process, showing there to be substantial benefits achievable through the adoption of PI. The conceptual PI plant has a reacting inventory five orders of magnitude smaller, and total inventory three orders of magnitude smaller than the existing reactor. Capital cost is

less than half the price of a new glass-lined stirred tank reactor. Benefits to the company of applying PI will involve safer process operation, improved product quality and increased productivity. A successful application of this individual plant design would give impetus to modernising the whole site, making it a cleaner, safer and more efficient place.

Future work will focus on the laboratory protocols section of the methodology. This involves further development of experimental equipment and procedures to demonstrate intensified, continuous operation. This is a vital part in proving the success of a PI concept and will allow determination of the benefits achievable, without the need for building a continuous pilot plant.

Awareness of PI still has to be raised in some sectors of the chemical industry, though there are signs that many firms are looking towards innovation as a means of gaining a competitive edge and meeting legislation. A change in the way process development is traditionally done will be required for innovation to be properly adopted. This PI methodology provides a mechanism to promote such a change by encouraging PI to be considered where it may normally be overlooked.

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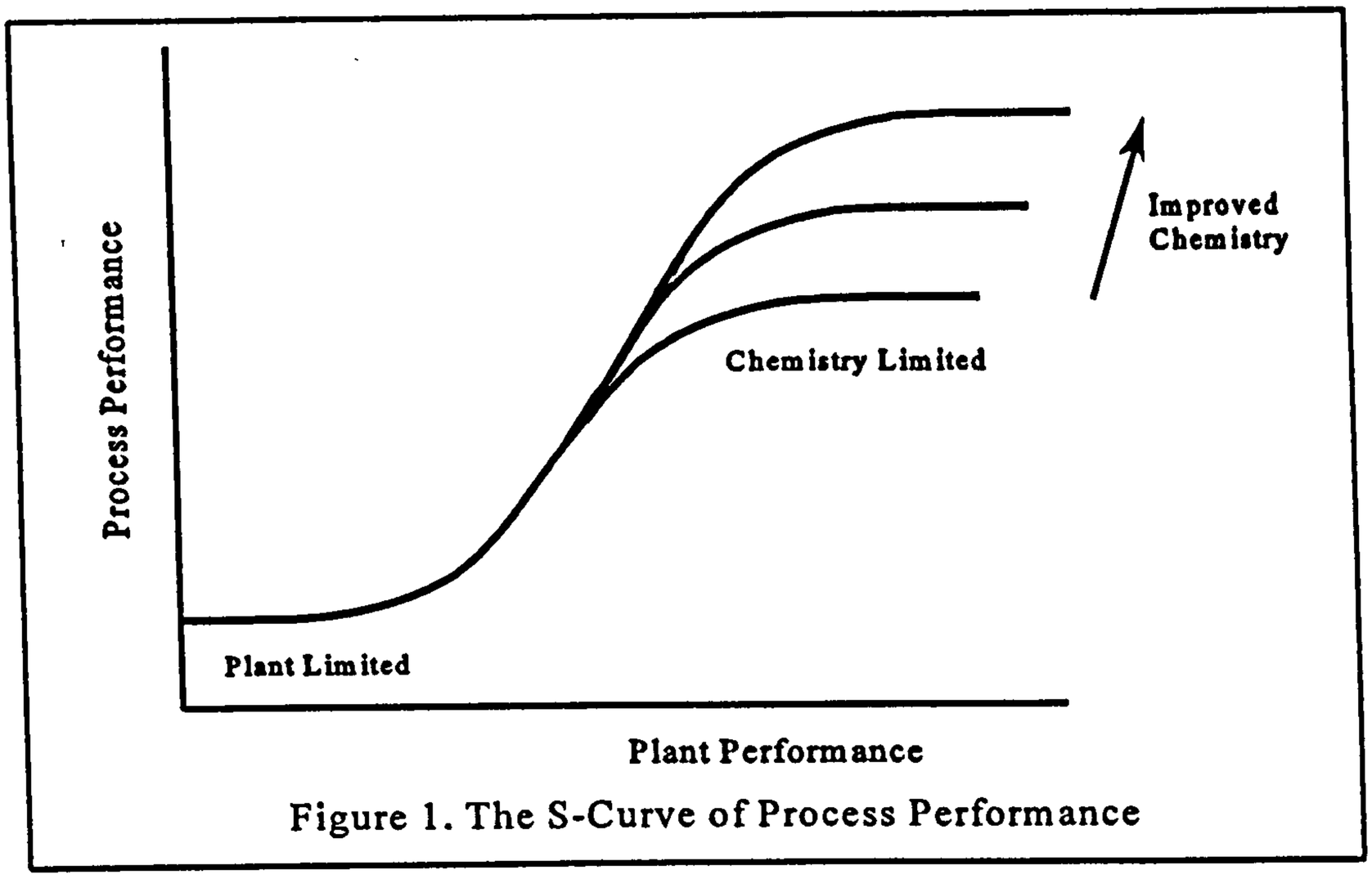

Figure 1. The S-Curve of Process Performance

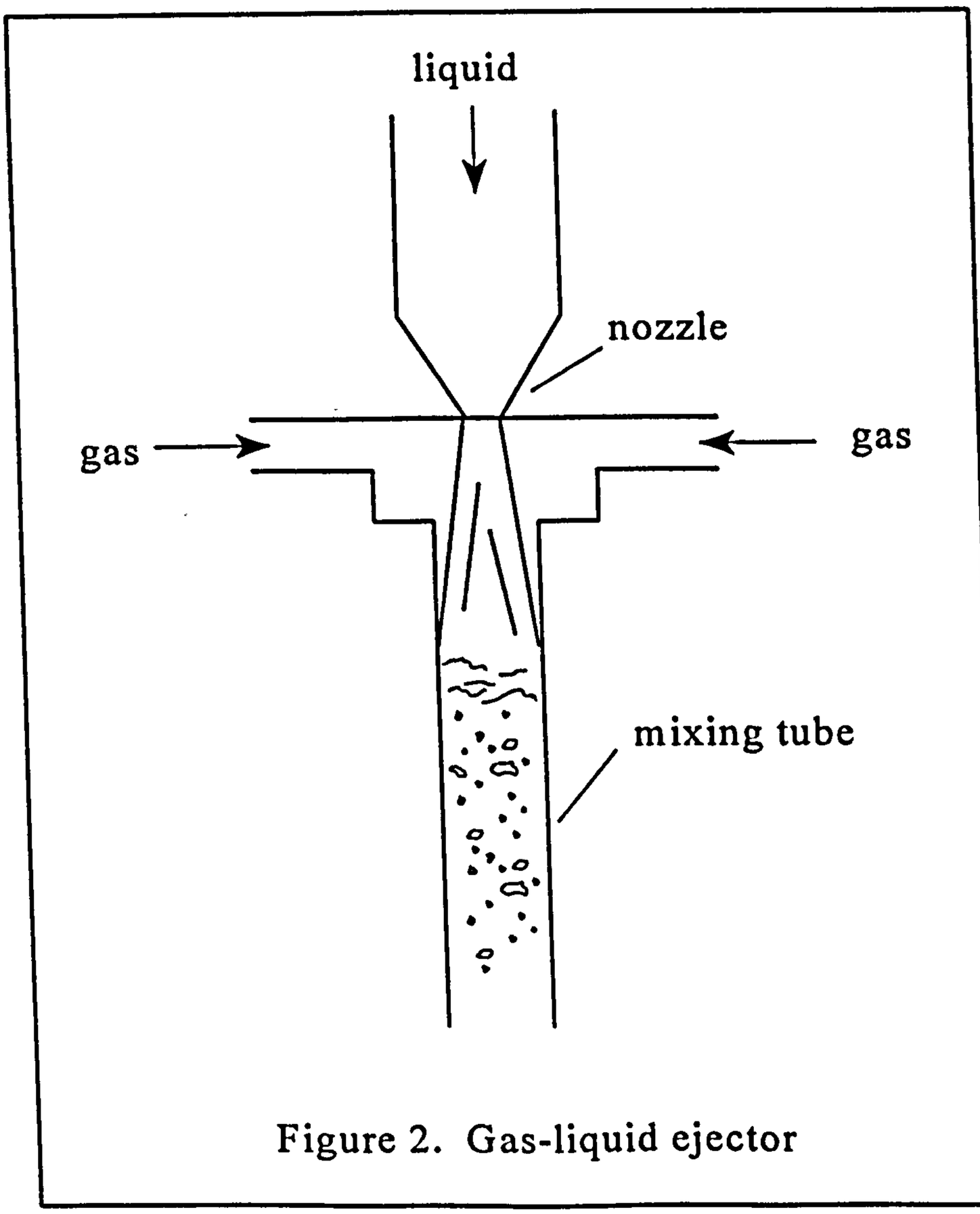

Figure 2. Gas-liquid ejector

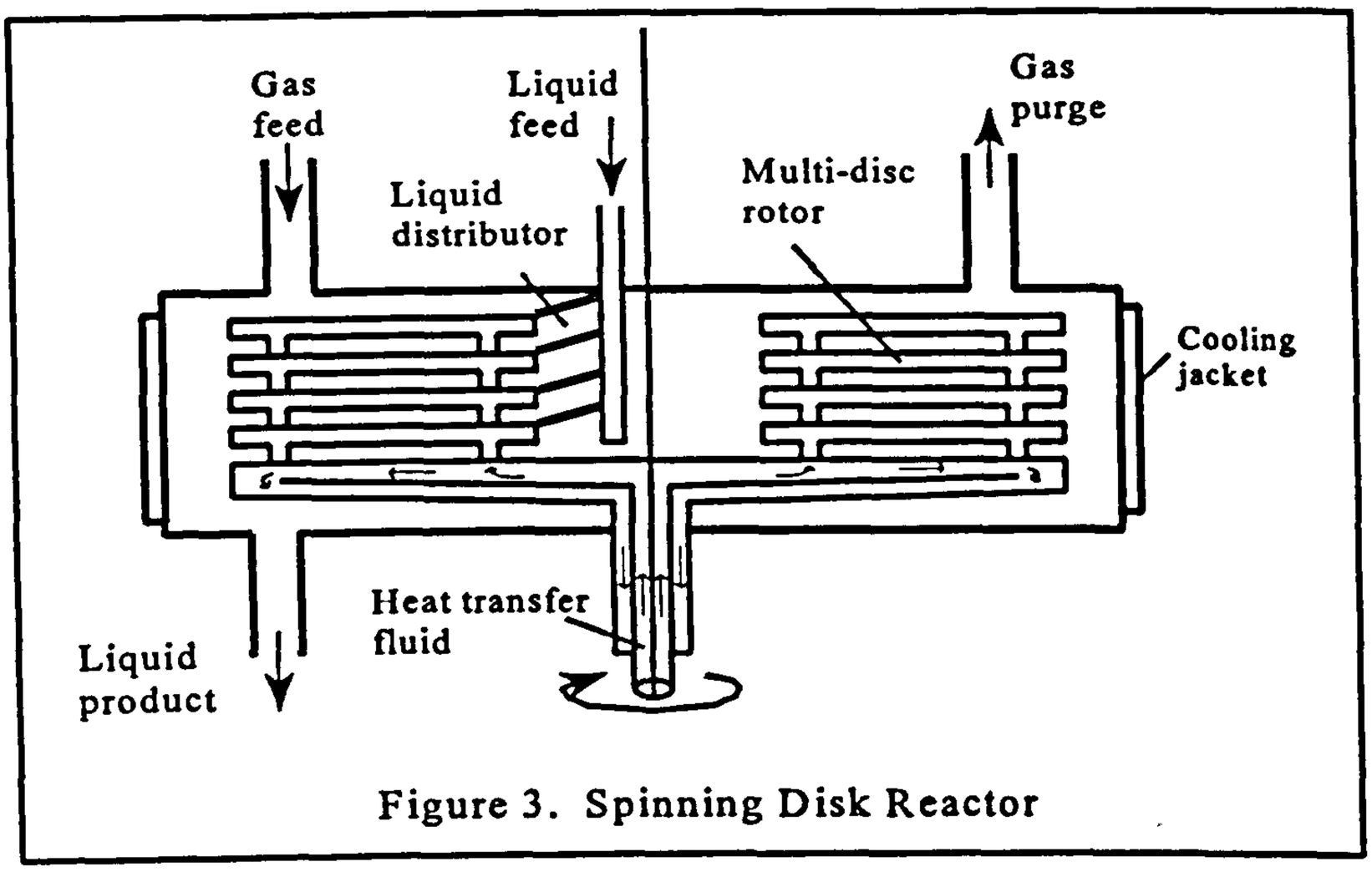

Figure 3. Spinning Disk Reactor

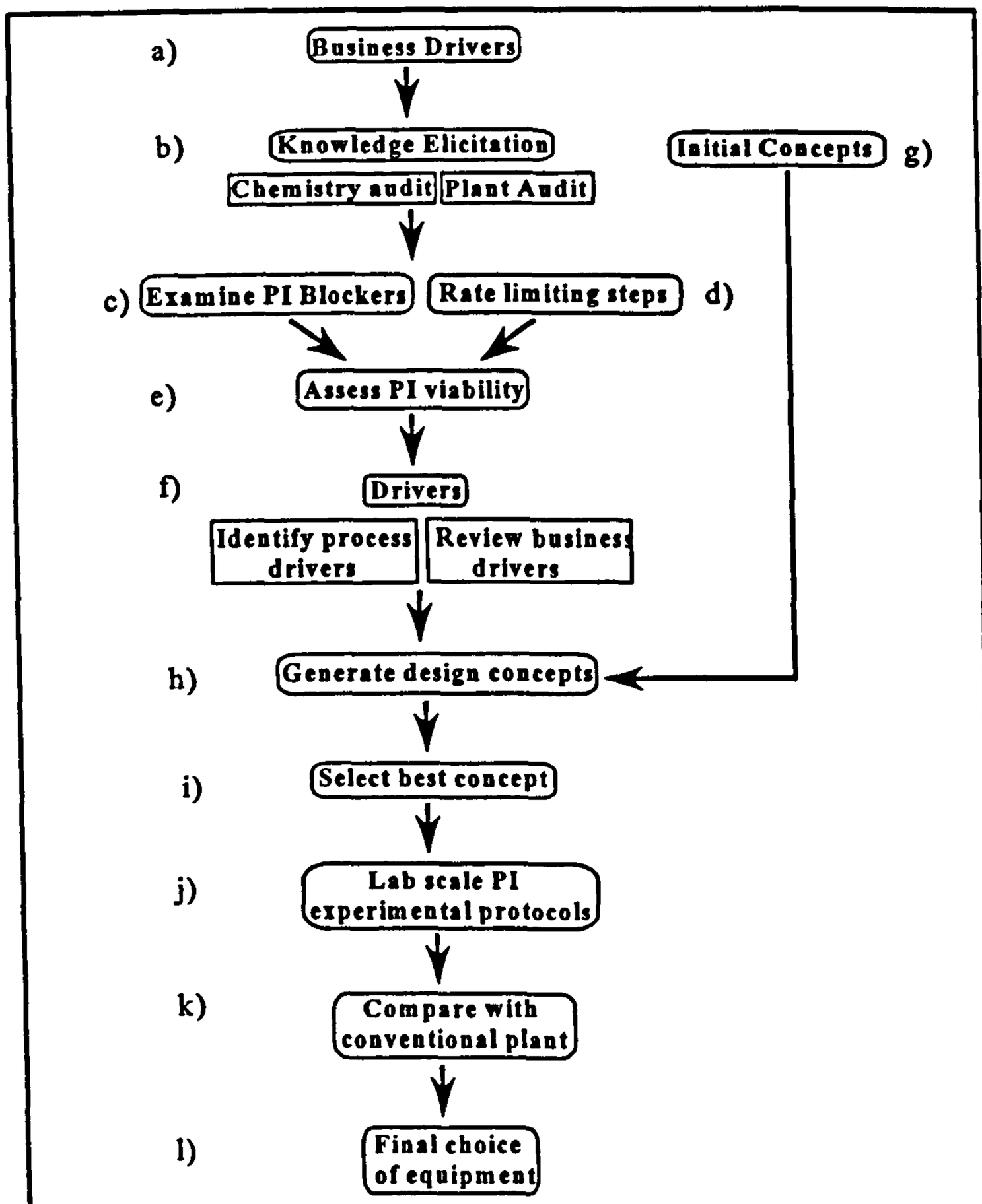

Figure 4. Methodological Approach to PI Applications

Figure 5. Scale drawing of existing stirred tank reactor and proposed PI reactor

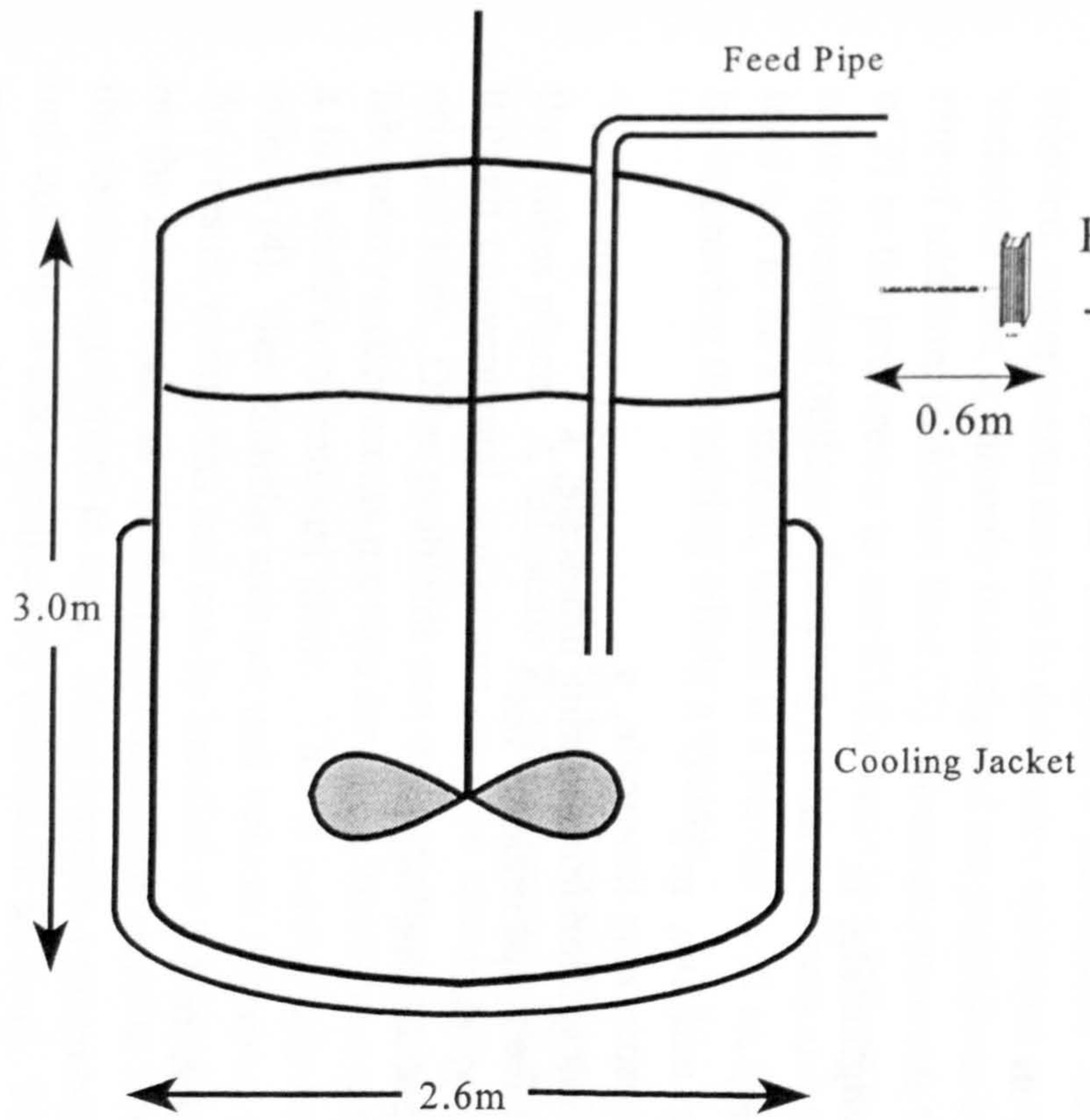

Figure 5(a) Existing Stirred Tank Reactor

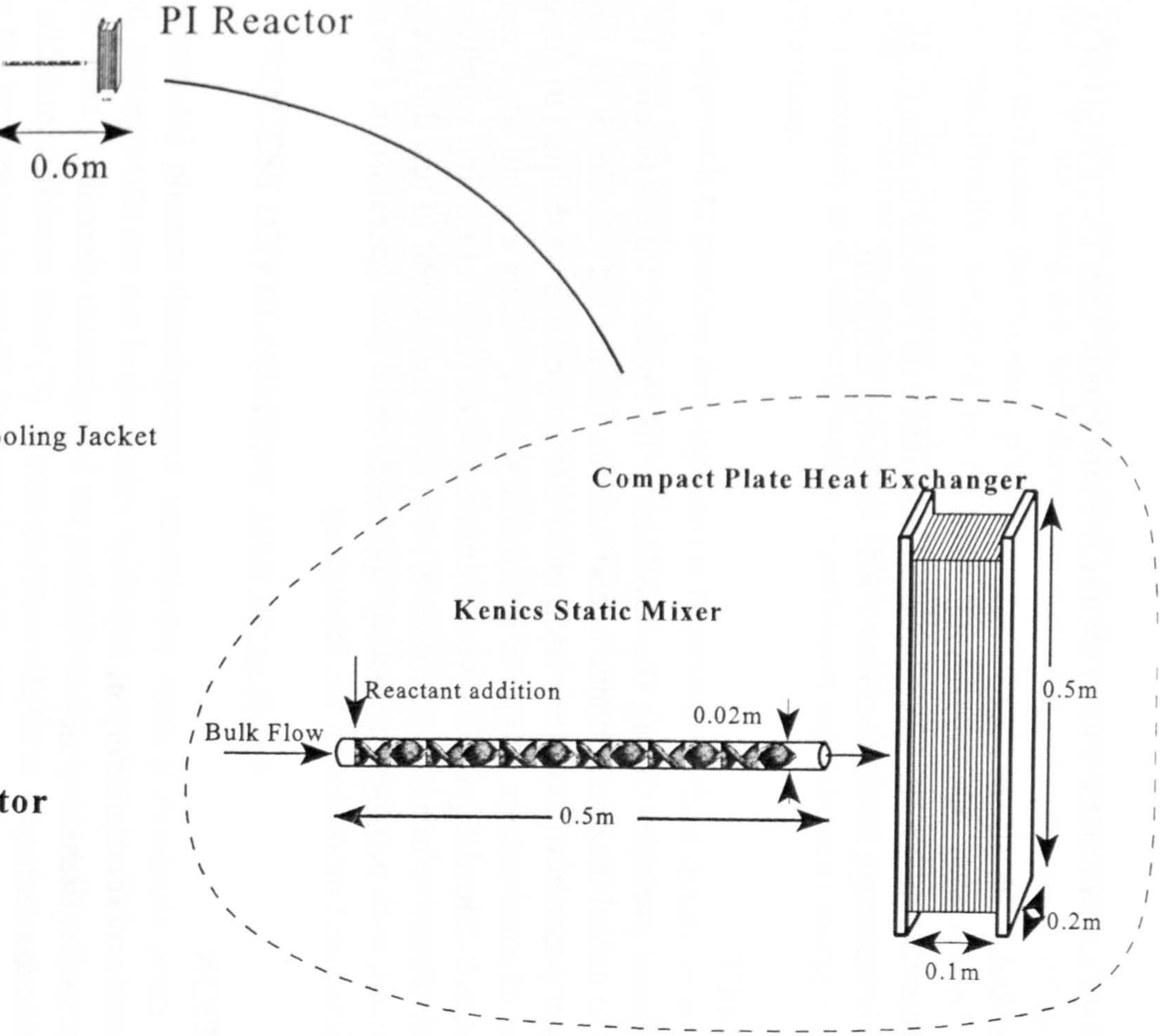

Figure 5(b) Proposed PI Reactor

D.3 LABORATORY PROTOCOLS FOR PROCESS INTENSIFICATION

MD Wood, AJ Green, JM Kay

Paper presented at the 3rd International Conference on Process Intensification for the Chemicals Industry, 25-27 October 1999, Antwerp, Belgium.

ABSTRACT

A significant problem facing the application of Process Intensification (PI) is the inability to model the performance of con`tinuous, intensified reactors in the laboratory. This paper describes laboratory equipment and procedures developed to simulate the operation of static mixers, a type of intensified reactor, within a small scale semi-batch stirred vessel. The design of the vessel allows a wide range of mixing conditions to be produced. Reactive mixing experiments have been carried out to test the performance of the vessel, with mixing correlations applied to show how operation in a PI plant can be predicted and modelled in the laboratory.

NOTATION

d	static mixer diameter, m
D	impeller diameter, m
f_D	friction factor, -
L_D	turbulent dispersion lengthscale, m
N	impeller speed, s^{-1}
P_o	impeller power number, -
Q_B	volumetric flow rate of additive, m^3s^{-1}
t_D	turbulent dispersion mesomixing timescale, s
t_S	inertial convective disintegration mesomixing timescale, s
u	velocity of fluid in the feed pipe region, ms^{-1}
$\bar{u}$	superficial fluid velocity, ms^{-1}
ϵ	turbulent energy dissipation rate, Wkg^{-1}
η	turbulence efficiency, -
θ	static mixer voidage, -
ρ	fluid density, kgm^{-3}
ν	fluid kinematic viscosity, m^2s^{-1}

1. INTRODUCTION

Process Intensification (PI) can provide many benefits to the chemical industry, including smaller, safer and cheaper chemical plant. Despite these benefits, application of PI technology is not widespread for a number of reasons, particularly unwillingness to take a risk with novel equipment (1). Preference is instead put on operation in stirred tank reactors (STRs), which are widely available and familiar technology. Another

significant barrier is the inability to model PI in the laboratory, resulting in the potential for applying PI not being explored during the early stages of process development when it can most influence the eventual plant design. This shows the need for experiments that are specifically designed to recreate the conditions experienced within PI equipment. The experimental modelling should serve two main purposes: firstly to show that intensified operation provides real benefits in terms of product quality and yield, and secondly to simulate operation in particular equipment to increase confidence in PI operation.

The PI approach to process development is to provide a fluid dynamic environment that matches the needs of the chemical process, so that performance is dictated by intrinsic chemical kinetics rather than being physically limited (2). This paper introduces the theory and practical considerations of designing laboratory experiments to model the fluid environment delivered by PI equipment. A small scale, intensively mixed stirred vessel has been designed to investigate whether it is possible to recreate and predict the performance of continuous, intensified plant in the laboratory without the need for building costly continuously operating equipment.

2. PROCESS DEVELOPMENT AND SCALE-UP

In conventional process development procedures, once a synthesis route has been selected, experiments are run to determine optimum operating conditions. The process variables most commonly investigated are stoichiometry; concentration; temperature; rate of addition; residence time (3). These experiments form a barrier to the application of PI as the preference to use STRs leads to a failure to run experiments that consider other operating options. Crucially, mixing effects and the fluid dynamic environment tend not to be examined, which is a barrier to PI as this achieves many of its benefits by improving the mixing within a system.

Scale-up from laboratory to full scale operation to make more material per unit time then takes place. A full scale PI plant may be of similar size to the laboratory tests, though conventional equipment may be many orders of magnitude larger than the original tests. Often problems can occur during the large volume scale-up to STRs as laboratory experiments provide far more intensive conditions than those achieved by a full scale conventional plant. This is particularly true for heat and mass transfer effects (4). Heat transfer area per unit volume decreases as a stirred tank size increases. As a result, exotherms that can be handled in the laboratory may become rate-limiting on the large scale as the feed, and therefore reaction rate, have to be reduced to allow the cooling equipment to cope. Mass transfer, represented by mixing energy input per unit volume, is also significantly reduced on scale-up. The result is that product quality may suffer and processing times increase significantly between laboratory and large scale operation.

The problems facing PI when scaling-up from the laboratory are the opposite to those faced during conventional scale-up. To achieve a fluid dynamic environment that allows the reaction to run at its inherent kinetic rate, very rapid mixing may be required.

This is obtained through the input of a high mixing energy. However, the very same traditional laboratory experiments that provide too high a mixing intensity for conventional scale-up cannot provide a high enough mixing intensity to model PI operation.

Trambouze (5) identifies that development experiments should ideally be "..designed to simulate the industrial reactor. In other words, the real problem lies in scale down, rather than scale-up". This requires the development of small scale equipment whose performance matches that of the large scale plant, whether conventional or intensified. This approach would reduce the potential for problems occurring on scale-up.

In this research, laboratory procedures, known as protocols, have been designed to match the mixing performance of full-scale intensified plant items. The static mixer has been chosen as the equipment to base the modelling investigations upon. Static mixers are pipe inserts that promote mixing and turbulence and are a simple type of PI mixing technology that has already achieved applications for blending and reacting duties. Figure 1 illustrates a Kenics type static mixer.

3. MIXING THEORY

PI operates by matching the fluid dynamic environment of the plant to the needs of the process. This fluid dynamic environment can be described by different mixing mechanisms. Three major scales of mixing have been identified (6):

Macromixing	Large scale blending throughout a vessel
Mesomixing	Mixing of an additive from a feed pipe with its surroundings
Micromixing	Molecular scale mixing prior to reaction

3.1. Specific Energy Dissipation

Each of the above mechanisms have mixing timescales that depend upon the mixing power input into the system. This power input can be expressed as the specific energy dissipation rate, ϵ, with units of power per unit mass of inventory (W/kg). For a stirred vessel, the average specific energy dissipation is determined by:

$$\epsilon = \frac{P_0 \, \rho \, N^3 \, D^5}{mass} \qquad (1)$$

Approximate values for P_o, the impeller power number, are: 5 for Rushton turbines; 1.3 for pitched blade turbines; 1 for propellers. N and D are the impeller speed and diameter.

Energy dissipation in static mixers results from pressure drop being converted into mixing energy through generation of turbulence. Different types of static mixer convert

different proportions of the total energy dissipation into mixing energy. The fraction converted is known as the turbulence efficiency, η. Typical static mixer efficiencies are 50-80%, with the specific energy dissipation rate determined from (7)

$$\epsilon = \eta \left(\frac{f_D \, \vec{u}^3}{2 \, d \, \theta} \right) \qquad (2)$$

The Darcy friction factor, f_D, varies widely between different mixer types, but is approximately 2 for the Kenics type mixer. Mixer voidage, θ, is approximately 0.9 for most mixers. Static mixers produce energy dissipation rates in the range 1-1000 W/kg with good overall mixing homogeneity throughout the mixer volume. These values of ϵ are much higher than can be achieved in large stirred tanks. Butcher and McGrath (8) state that the average value of ϵ in STRs is 1-10 W/kg, with a variation in ϵ of 50:1 between different regions being common, particularly between the impeller and surface of the liquid. This mixing inhomogeneity can result in variations in product quality depending upon where feed is added.

3.2. Mixing correlations

Mesomixing and micromixing are the most relevant mechanisms to reactive mixing when reaction kinetics are fast, which is when PI is most applicable. Correlations and mixing models, described below, enable estimation of mixing timescales for both stirred vessels and static mixers. These models are presented here in their simplest form for the purposes of this study.

Mesomixing describes the breaking down of an additive stream from a feed pipe into the bulk liquid flow. It is larger in scale that the micromixing that brings molecules together for reaction, but is on a far smaller scale than macromixing that relates to blending throughout the entire vessel. Two different mesomixing models have been developed (9): turbulent dispersion of a feed stream and inertial convective disintegration of large eddies.

In turbulent dispersion, the feed stream spreads out transverse to its local streamline. For stirred tanks, the following correlation can be derived for the turbulent dispersion characteristic timescale (10):

$$t_D = \frac{Q_B}{0.124 \; u \; \epsilon^{1/3} \; L_D^{4/3}} \qquad (3)$$

Q_B is the flow rate of additive through a feed pipe. The characteristic length scale of turbulent diffusivity, L_D, is related to the size of the turbulence eddies. The length scale should be greater than the feed pipe diameter, but has also been identified as being 0.52w, where w is the height or projected height of the impeller blade (10). Local flow

velocity, u, has been found to be approximately 0.25 x impeller tip speed for a Rushton turbine in the impeller region (11). It is also possible to estimate u through the use of the impeller flow number, which is a constant value and is defined as the flow through the impeller divided by ND^3, where N and D are the impeller speed and diameter. The flow rate can be divided by the swept area to obtain an approximate fluid velocity in that region.

The second mesomixing mechanism is inertial convective disintegration. Large eddies of additive will disintegrate and be reduced by inertial action towards the micromixing scale. The following correlation can be applied to determine the mesomixing timescale under this mechanism (7).

$$t_s = 2.17 \left(\frac{Q_B}{u \epsilon} \right)^{1/3} \qquad (4)$$

Estimations and assumptions made in both of the mesomixing models mean the timescales calculated are only approximations, with Baldyga *et al* (9), stating "The approaches towards estimating meso-mixing time and length scales should be regarded as tentative".

Micromixing relates to molecular level mixing where chemical reaction takes place. The engulfment model of micromixing, described by Baldyga & Bourne (12), can be applied to both stirred tank and static mixer operation. ν is the kinematic viscosity of the fluid.

$$t_{micro} = 17.2 \left(\frac{\nu}{\epsilon} \right)^{1/2} \qquad (5)$$

4. MIXING SENSITIVITY IN CHEMICAL REACTION SCHEMES

Varying the mixing intensity and therefore rate of mixing can affect the product quality of competitive reaction schemes. This effect is known as mixing sensitivity, and can be used to illustrate how PI achieves some of its benefits. The azo-coupling reaction scheme is a mixing-sensitive competitive parallel and consecutive scheme that has been used to characterise mixing within intensified and conventional reactors. The scheme is outlined below, with full details given by Baldyga and Bourne (13).

$$A + B \xrightarrow{k_1} R \qquad \text{desired reaction}$$

$$R + B \xrightarrow{k_2} S \qquad \text{consecutive}$$

$$C + B \xrightarrow{k_3} Q \qquad \text{parallel}$$

$$k_1 > k_2 > k_3$$

A and C are 1- and 2-naphthol respectively. B is diazotised sulfanilic acid. Product R is defined as the desired product and is formed by the fastest reaction, with S and Q being akin to byproducts. The yield of byproduct Q, X_Q, is used to characterise the degree of mixing within the system. The product yields can be determined through spectrophotometry, from which the mixing intensity within the system at the time of reaction may be inferred.

The limiting reactant, B, is added to bulk reactants A and C. In semi-batch operation, this addition occurs over a period of time with the reaction taking place in a volume known as the reaction zone. Slow feeding, or low feed flow rate Q_B, results in a very small B-rich zone that rapidly mesomixes with the surrounding fluid, leaving micromixing as the limiting mechanism. This is known as micromixing control and produces the minimum amount of byproducts formation through reaction of B with C and R. Increasing the feed rate results in a larger B-rich zone in the area of the feed pipe that requires longer to mesomix than micromix, resulting in mesomixing control. This increases the length of time reactant B is in contact with C and R in the reaction zone and hence increases the waste production. Increasing the mixing intensity decreases both the meso- and micromixing timescales, reducing the byproduct formation further.

As the feed rate in semi-batch operation is slowed down, mesomixing timescales are reduced relative to the micromixing timescale and waste yield reduces to an asymptote where the reaction becomes micromixing controlled. The point where this asymptote begins is the critical feed time, t_{crit}. Figure 2 illustrates this effect. Increasing the intensity of mixing, ϵ, in a stirred tank will shift the feed time curve downwards and towards the origin, thus reducing t_{crit} (14).

Continuous operation in static mixers is the equivalent of a very short feed addition time in Figure 2, as all the feed is added in stoichiometric amounts rather than over a period of time as happens in semi-batch operation. Under these circumstances static mixers are mesomixing controlled, unless the flow rate of additive is very low relative to the bulk flow rate. As a result, waste production is higher that would be achieved if micromixing was limiting. This has been demonstrated experimentally by Baldyga *et al* (9). However, the very high values of ϵ experienced within static mixers result in much lower values of X_Q than could be achieved in stirred tanks, despite the mesomixing control.

5. LABORATORY PROTOCOLS EQUIPMENT

Following the examination of mixing theory, it is concluded that any laboratory protocols should match not only the mixing intensity experienced within the static mixer, but also the characteristic mixing timescales. Two main options were explored for achieving this: building a small scale, continuously operating rig and using a versatile stirred tank.

To simulate continuous, intensified operation at the laboratory scale, the natural

approach would appear to be building a small scale continuously operating rig. This would demonstrate the equipment itself in operation and be particularly useful in building operating confidence in PI. However, static mixers are not flexible enough to handle a wide range of operating conditions and have to be tailored to particular reaction schemes. This can be overcome by building a rig with replaceable static mixer elements for testing different reaction schemes. However, this would add to the cost and complexity of the equipment. Also, if turbulent flow conditions need to be achieved, the pipe size and flow rate required are such that impracticably large amounts of feed would be consumed when running continuously for even a short period.

The most versatile piece of equipment for producing a wide range of operating conditions, is the stirred tank, which is why it is used so widely in the process industry. As a result, a stirred vessel design has been chosen for the protocols equipment. The vessel is 10cm in diameter and height, with a volume of 785ml. Four 1cm width baffles run the full height of the vessel to prevent swirling. A lid is fitted to the vessel to prevent the air entrainment and splashing that could result from high mixing speeds. A small chimney around the impeller entry hole provides a liquid seal when filled to a depth of only a few millimetres. The presence of the chimney means that a small proportion of the overall vessel volume, approximately 1%, will not be subject to the same mixing intensity as the bulk liquid, but this is not expected to affect the overall performance significantly. The equipment is currently limited to adiabatic operation.

The impeller selection and arrangement were based upon the requirement for homogenous mixing combined with high power input. A pitched blade turbine (PBT) was selected as this is an axial flow impeller and will distribute mixing power input more evenly throughout the vessel than a radial flow impeller, such as the Rushton turbine. Mixing homogeneity can be improved through the use of dual impellers, so two 3-blade PBTs are utilised, spaced equally along the impeller shaft. Relatively large diameter impellers, D=6cm, were chosen as they provide both high power input (proportional to D^5, Equation 1) and more homogenous energy dissipation than smaller impellers. The dual impeller power number was measured as being 1.8, and the flow number was calculated to be 0.82 from the results of previous experimental tests on impeller systems (15).

Mixing speeds of up to 2600 rpm are possible with the mixer used for the protocol experiments. From Equation 1, this equates to a maximum energy dissipation rate of 150 W/kg, which is comparable to the mixing intensities achievable in static mixers. Feed is added via a burette that allows a smooth addition of the small volumes of feed required. The feed pipe diameter is 0.5mm to prevent backmixing into the feed pipe, which was found to occur in a 1mm diameter feed pipe at higher mixing intensities.

Figure 3 shows the design of the vessel. It also illustrates the homogeneity of the mixing by showing the experimentally obtained mixing intensity divided by the mean vessel mixing intensity at a variety of axial locations. The highest mixing intensity ratio is around eight times the lowest ratio, which is far better than the typical 50-fold variations experienced in other stirred tanks (8). Even in static mixers, variations in mixing intensity of 4-fold have been noted across individual elements (7). Therefore

the protocols vessel design provides an acceptable uniformity of mixing. Subsequent experiments added the feed between the two impellers, as this area is subject to the mean vessel mixing intensity.

6. EXPERIMENTS TO INFER THE POTENTIAL FOR INTENSIFICATION

The first objective of the PI laboratory protocols is to show that intensified operation can achieve real benefits. Reactions with the fastest kinetics benefit most from the rapid mixing and short residence times of PI equipment. Mixing sensitivity characteristics can be used to infer chemical reaction rates if the kinetics of a reaction scheme are not known, as is often the case (3).

The following tests could be carried out in well-mixed equipment, such as the vessel described above, using semi-batch addition with a set feed time. If the kinetics of a competitive reaction scheme are much slower than the mixing timescales within a vessel, the reactants will be fully blended before reaction occurs, so varying the mixing intensity will have no effect on product yield. Intermediate speed reactions will produce a varying product yield up until a certain level of mixing where mixing rate becomes faster than reaction rate. This will give an indication of the level of mixing required to achieve a desirable product quality. It is possible that reactions will be so fast that no upper mixing limit is achieved as the mixing timescales cannot be brought low enough to allow the reaction to become kinetically controlled. If a high mixing intensity is shown to produce benefits in product quality and yield, this would indicate that PI would be an advantage for the system.

Feed time effects should also be examined. The feed time curve, figure 2, shows that up until a critical feed time, waste yield decreases until the micromixing is the limiting mechanism. This information is required at a variety of mixing intensities for the subsequent section of the protocols approach.

7. SIMULATION OF STATIC MIXERS

Static mixers tend to be mesomixing controlled under many operating conditions. Semi-batch operation is also mesomixing controlled when operating below the critical feed time. At a given mixing intensity, the micromixing timescale will be the same for both the stirred vessel and static mixer, from Equation 5. Therefore the protocols approach tested was to determine whether the azo-coupling product yield at a certain mesomixing timescale will match the yield obtained from a static mixer at the same mixing intensity and mesomixing timescale.

Experiments have previously been carried out at BHR Group on a 32mm diameter Sulzer SMXL static mixer operated at four mixing intensities of 8, 26, 61 and 118 W/kg (16). The flow ratio used of bulk A and C to B of 150 is the equivalent of a 5.2 ml addition to the vessel. Using the identical chemical make-up as in the static mixer tests,

the vessel was operated at the four mixing intensities with a variety of feed addition times to generate mixing sensitivity curves.

There are two mesomixing timescale models: turbulent dispersion, t_D, and inertial convective disintegration, t_S (Equations 3 and 4). During operation in static mixers, the inertial convective disintegration timescale is significantly longer than turbulent dispersion timescale and is hence the controlling mechanism. However, both models have a similar timescale when applied to a stirred vessel, so should be considered together to determine which is the limiting mechanism. Consequently, the experimental results have been plotted as X_Q against both t_D and t_S in Figures 4-7, with the static mixer X_Q value plotted against t_S only at each mixing intensity.

Varying the value of L_D to fit the dispersion model results to the static mixer results found that if L_D is set at 1.1mm, then all of the linear trend lines for the dispersion model pass close to the static mixer experimental result at the same mixing intensity. The feed time required to achieve the same mesomixing time in the vessel as in the static mixer was approximately 5 seconds for all mixing intensities. Convective disintegration model results are set to the left of the dispersion model results, showing that the convective disintegration timescale is the shortest and hence turbulent dispersion is the controlling mesomixing mechanism in the vessel.

The comparisons between the vessel and static mixer suggest that there is indeed a connection between experimental results in a semi-batch vessel and the static mixer. The L_D value of 1.1mm determined here may differ at other concentrations and viscosities and so further tests are required to examine this possibility. 1.1mm may also not be the actual turbulent dispersion length scale, but rather an inferred length scale that includes any inaccuracies in the approach taken to comparing semi-batch with continuous operation. Again, this will require further experimental testing and verification under a range of different reaction conditions.

8. DESIGN PROCEDURES

Although experimental verification of the protocols approach is limited to four experimental points, procedures can be set out for designing an appropriate static mixer or determining the performance of a particular static mixer design by using the protocols approach. During process development, mixing sensitivity tests should be carried out using the protocols vessel, with yield plotted against turbulent dispersion mesomixing timescale at different mixing intensities and feed times. If mixing sensitivity occurs, this will indicate the potential for intensification, possibly via static mixer operation, subject to consideration of potential PI blockers that may otherwise prevent the application of PI (17).

Any static mixer design depends upon achieving a certain production objective without entailing excessive energy requirements. When selecting an appropriate design, the mixing sensitivity curves can be used to determine the range of mixing intensities and mesomixing timescales that can achieve the desired product quality, with a low

energy dissipation rate being preferable. From Equations 2 and 4, the static mixer diameter and velocity at this mixing intensity to achieve the required mesomixing timescale can be determined, leading to an appropriate static mixer design. Production targets may set the flow rate required from the static mixer, meaning the diameter and velocity are dependent variables.

If an existing or proposed static mixer design is required to be modelled, then a similar approach can be used to determine the mixing intensity and mesomixing timescale for the static mixer. The appropriate mixing sensitivity curve generated at the same mixing intensity can then be used to read off the product yield at the required mesomixing timescale.

9. CONCLUSIONS

Protocols have been developed to overcome the current inability to model PI in the laboratory. Mixing theory shows how PI can improve reaction yield by limiting the opportunity for byproduct reactions to occur. The protocols stirred vessel design allows a wide range of mixing conditions to be generated with a relatively homogenous mixing intensity. Experimental results show that if the turbulent dispersion model mesomixing length scale is estimated to be 1.1mm, then the stirred vessel matches the performance of a static mixer. A more rigorous study is required, examining the effects of concentration and viscosity upon the estimated mesomixing length scale for a variety of static mixer types and diameters. However, these preliminary findings can still be used to set out procedures to model the performance of static mixers without the need for building continuously operating experimental equipment.

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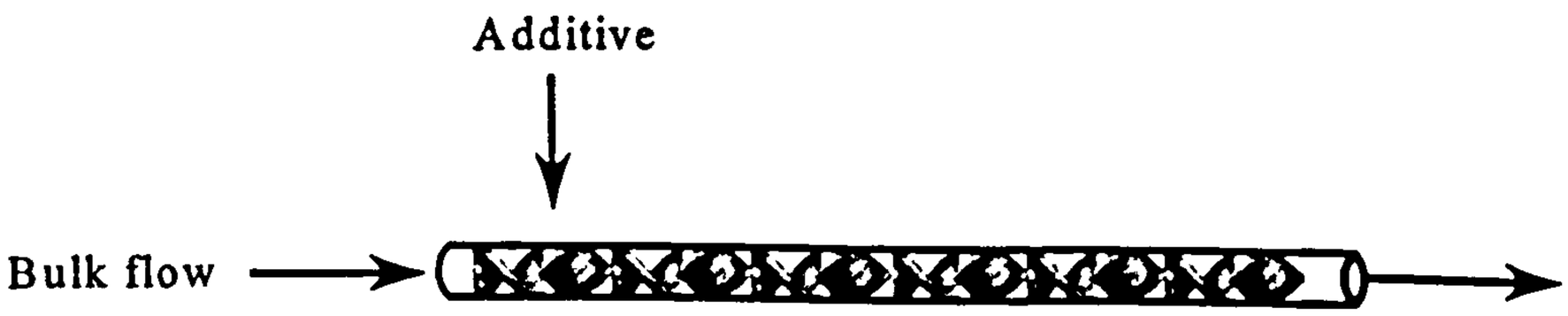

Figure 1. Kenics static mixer

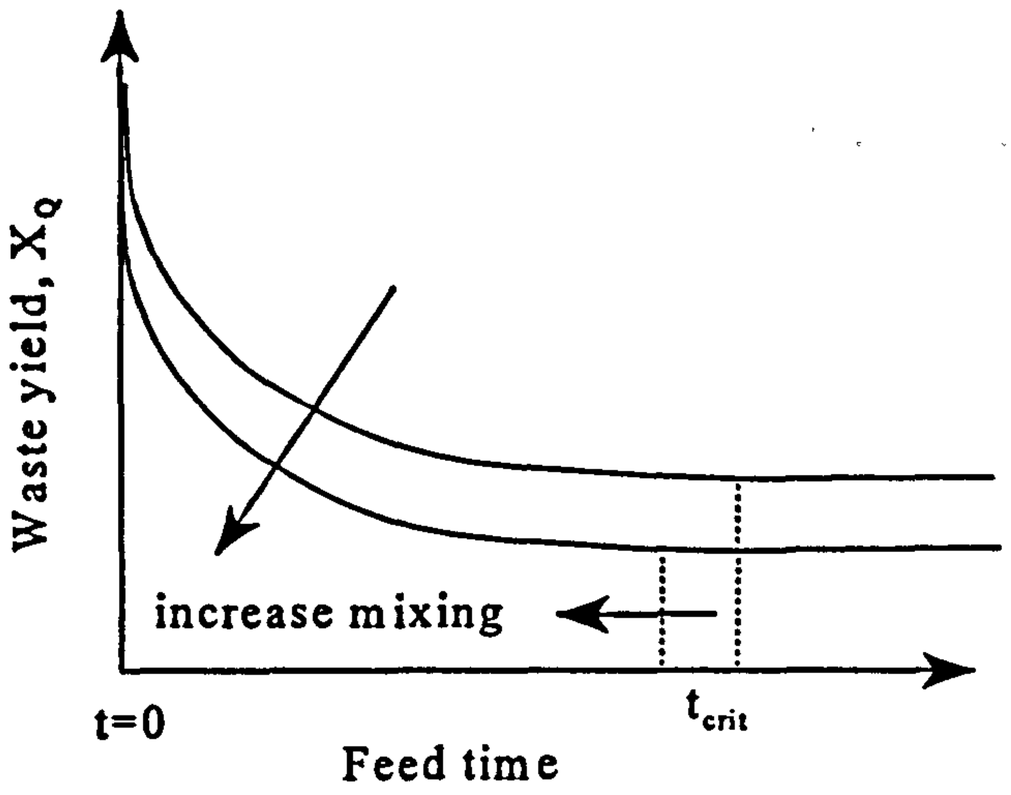

Figure 2 Feed time effects in a stirred vessel

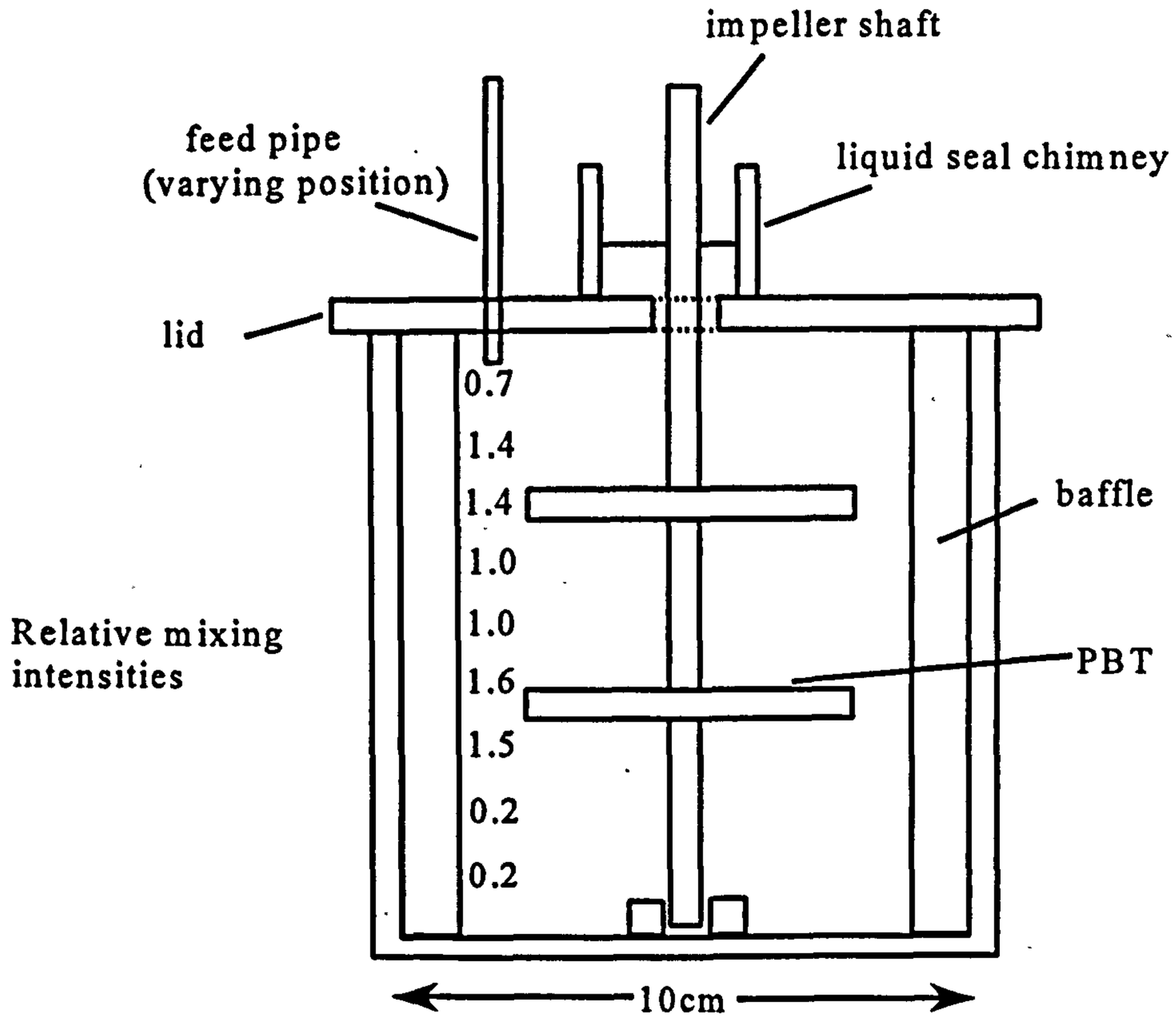

Figure 3. Laboratory protocols vessel

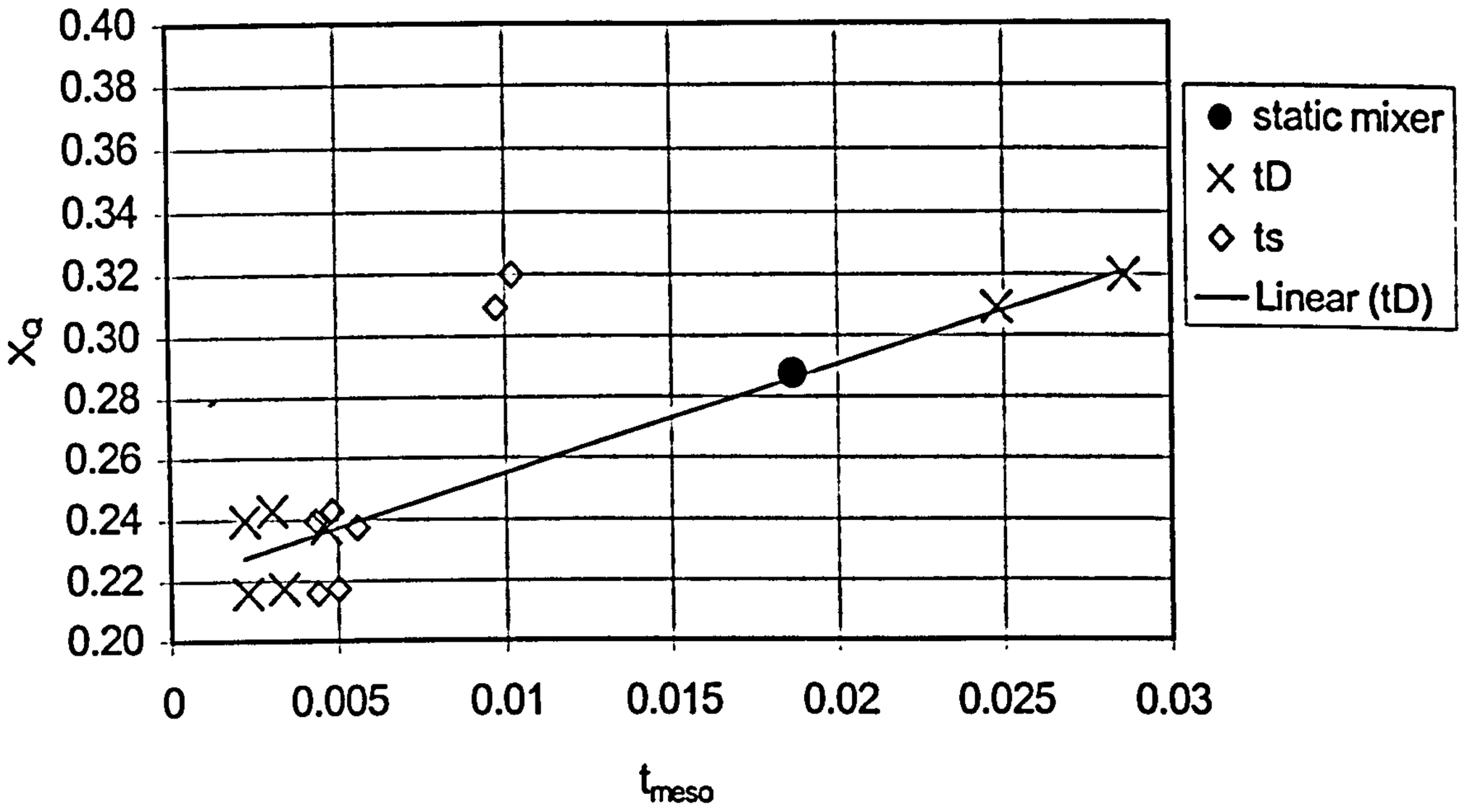

Figure 4. 8 W/kg

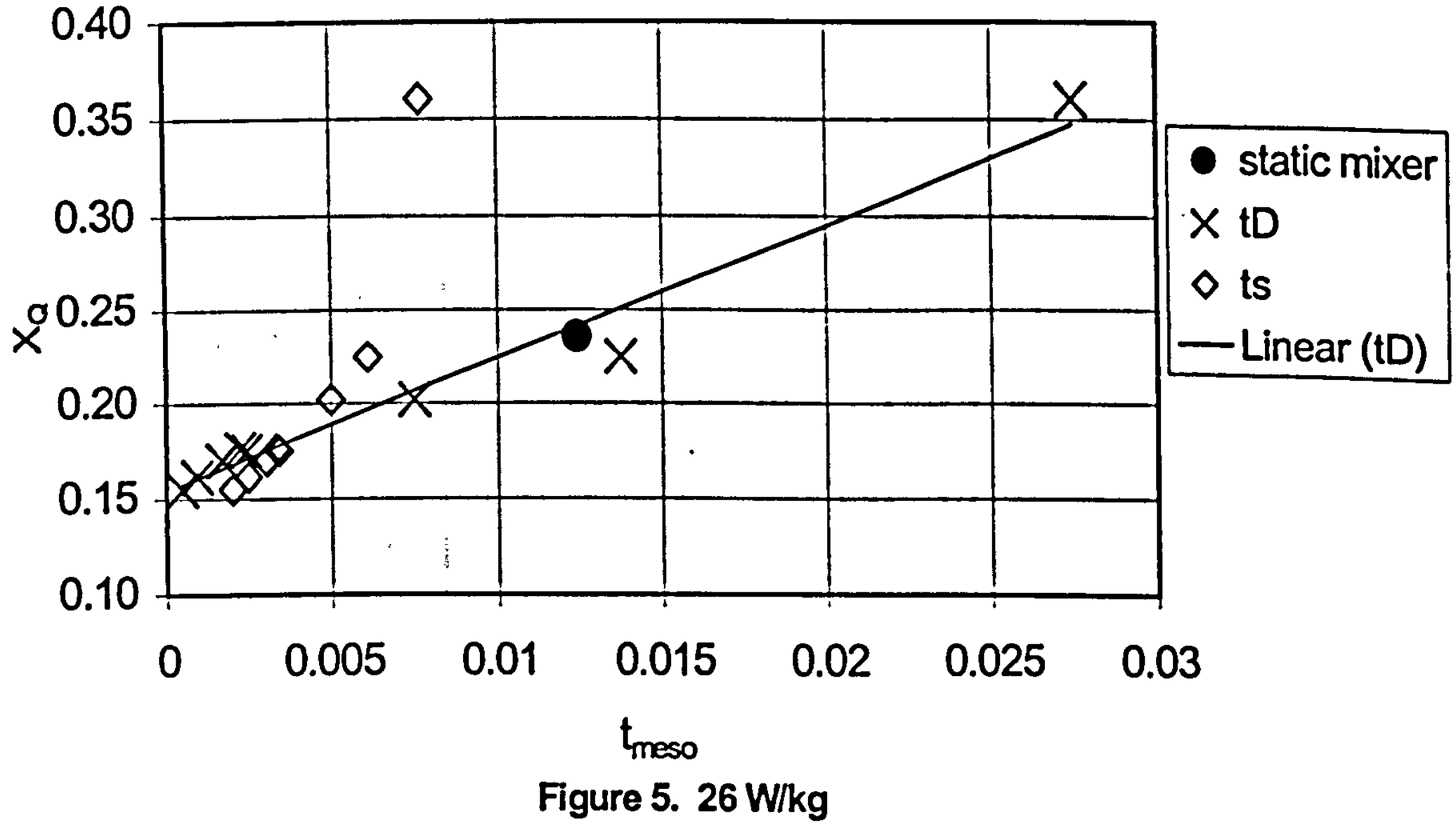

Figure 5. 26 W/kg

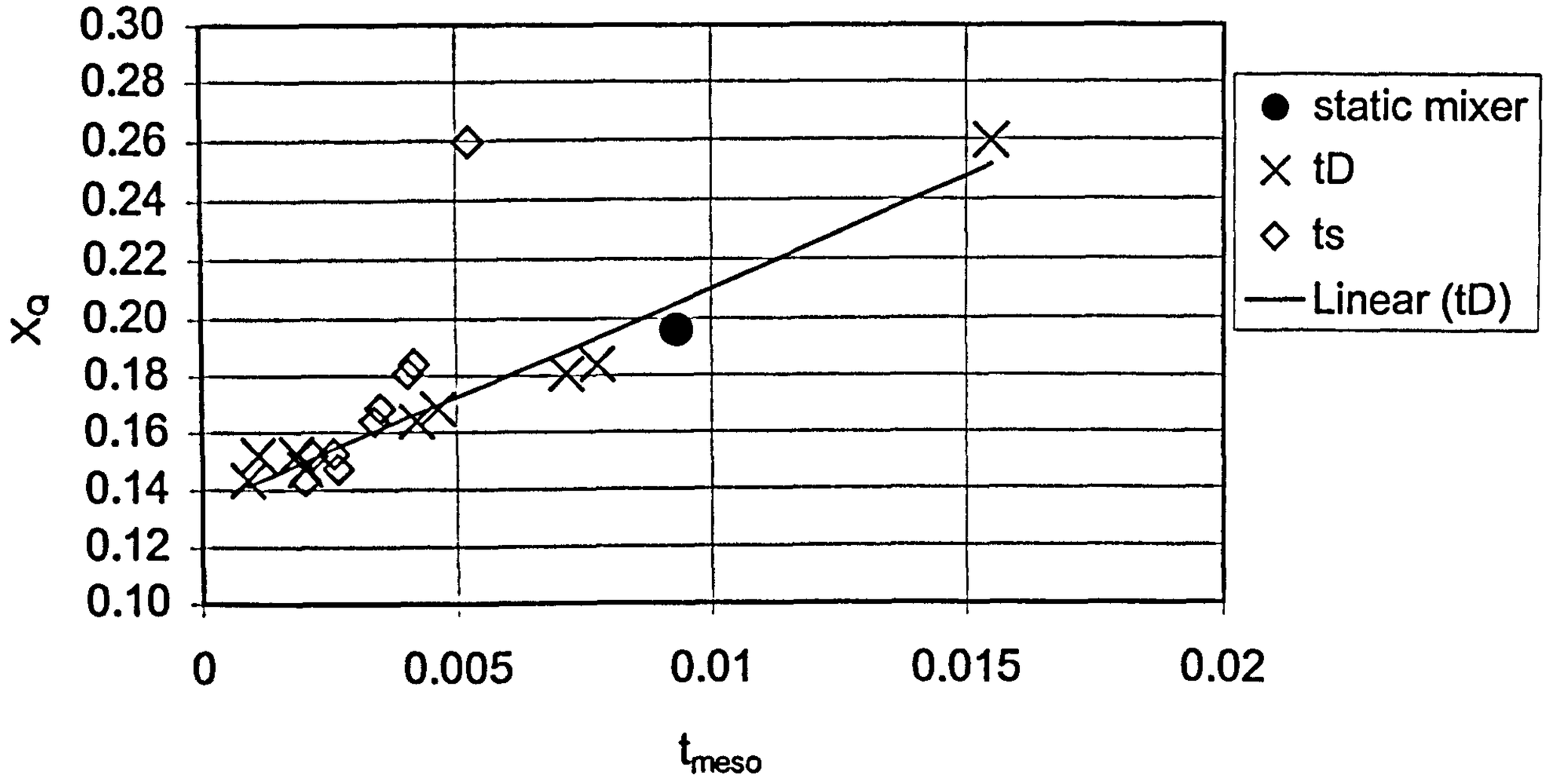

Figure 6. 61 W/kg

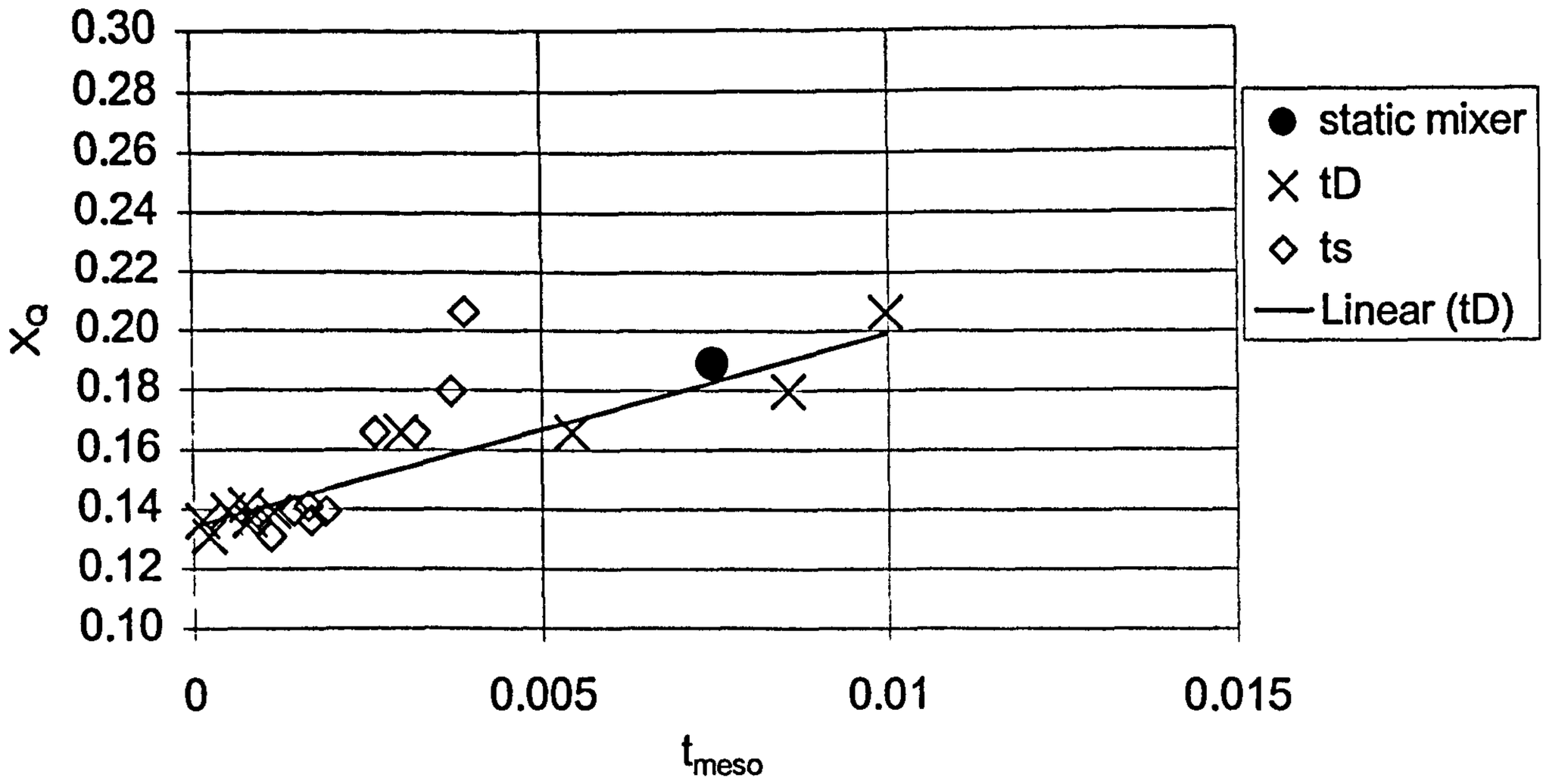

Figure 7. 118 W/kg